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RELATIVE DETERMINATION OF THE ATOMIC WEIGHT OF CHLORINE IN BAMLE APATITE

By Margot Dorenfeldt Received October 3, 1922

Introduction

This work was undertaken at the suggestion of Dr. Ellen Gleditsch in connection with an investigation carried out by Gleditsch and Samdahl, the object being to determine whether, in an old mineral which has not been in contact with water, the two chlorine isotopes of atomic weights 35 and 37 occur in the same proportion as in ordinary chlorine. The mode of attack was to compare the specific gravities of saturater colutions of sodium chloride, one solution being made from ordinary sodium chloride and the other from Bamle apatite, the method being similar to that described by Fajans and Lembert.²

Apparatus and Materials

The pycnometer was an exact copy of one described by Fajans and Lembert, a modified Sprengel-Ostwald type. The temperature variations of the thermostat cannot be given accurately but a 0.1° thermometer showed no change. The glass test-tubes in which the solutions were rotated in the thermostat were of thick glass, 14 cm. long, and of 22 mm. internal diameter. The clean tubes and the rubber stoppers were soaked in warm brine solution for 12 hours, after which treatment they were carefully rinsed. The balance was a Bünge with a sensitiveness of 0.4 mg.; no mirror was used but ½ divisions could easily be read.

The "ordinary sodium chloride" was a commercial highly purified preparation which was further purified. A saturated solution was treated with chlorine, the excess chlorine removed by boiling, the salt precipitated with hydrogen chloride, recrystallized

¹ Gleditsch and Samdahl, Compt. rend., 174, 746 (1922). Arch. Math. Naturvidensk., 38 (1923).

² Fajans and Lembert, Z. anorg. Chem., 95, 297 (1916).

evaporated to dryness, ignited, and recrystallized thrice. Weighing value No. 4, 1.202791, which agrees with that found for "ordinary sodichloride," 1.202791 and 1.202790.

After the work had been abandoned for a time the "apatite sodung chloride" solution was evaporated, ignited, recrystallized two or three times, and the specific gravity again determined (No. 5). Another evaporation, ignition and recrystallization gave value No. 6, the specific gravity of "ordinary sodium chloride" being determined at the same time.

The slight difference between the first and the last determinations of "ordinary sodium chloride" may be accounted for by a new setting the thermostat regulator. The measurements taken at the same te under identical conditions are in good agreement. Thus the averager "ordinary sodium chloride" under the earlier conditions agrees precise with the value for the purest "apatite sodium chloride" (No. 4), while later value, 1.202867, for "ordinary sodium chloride" agrees closs with the average, 1.202855, of the later values for the still further purifice "apatite sodium chloride."

A sample was then taken from each of the two solutions by means of the pycnometer and ignited to constant weight in platinum, all precautions being observed. When corrected to vacuum the "ordinary sodium chloride" weighed 3.31262 while the "apatite sodium chloride" weighed 3.31267 or 0.05 mg. more, a difference less than the errors of weighing (0.1 mg.). It follows that the atomic weight of the apatite chlorine does not differ from that of ordinary chlorine by an appreciable amount. Even if the solubilities found (26.357% at 18° or 35.790 g. per 100 g. of water) were not absolutely correct, the atomic weight 35.46 calculated from the relative values would still hold good.

Incidentally, we have compared the solubilities we found with those calculated from the formula of Andreae³ which are in good agreement with many recent determinations.⁴ The calculated value is 26.363%, while we found 26.357% which is in excellent agreement.

Summary

The chlorine isotopes in Bamle apatite occur in the same proportion as in ordinary sodium chloride.

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³ Andreae, J. prakt. Chem., 29, 467 (1884).

⁴ Taylor, J. Phys. Chem., 1, 718 (1896-1897). Berkeley, Phil. Trans., 203, 189 (1904). Fontein, Z. physik. Chem., 73, 212 (1910). Cohen, ibid., 75, (1912). Schreinemakers, Arch. Neer. sci. nat., 15.

Every method of measuring activity, except by the speed of reaction, depends upon the number of molecules passing through or reacting at a surface, which may be the surface of contact of the solution with a gas, with another liquid, with the solid form of the solute, or with an electrode. Since the activity is independent of the extent of this surface, it must be proportional to the number of molecules which collide with a unit surface. To account for different degrees of attraction of different surfaces, this may be expressed as the number which would collide with a unit standard surface multiplied by a coefficient for the particular surface. Also, the activity must be proportional to the fraction of colliding molecules that pass through or react at the surface, either of which we will call the fraction of reactive molecules. This may be summarized in mathematical form: activity = proportionality constant × number of collisions against unit standard surface × specific surface coefficient × fraction of reactive molecules.

In an ideal solution the fraction of the molecules that are reactive is independent of the composition, and the activity of each component is proportional to its mole fraction. So the number of collisions of each component is proportional to its mole fraction, and not in general to its concentration.

In collisions between 2 molecules, let us picture the molecules of the first type as colliding with those of the second. Then the number of collisions will be proportional to the mole fraction of the molecules of the first type. For a single molecule of the second type the factor of proportionality will be its surface expressed in equivalents of a unit standard surface, which will certainly depend upon the size and nature of its surface, and perhaps also on its motion through the solution. In an ideal solution, however, this factor will be independent of the composition. The total number of collisions in a liter will be proportional to the concentration of the molecules of the second type, the number per mole of each component to its mole fraction. In either case the number of collisions will be proportional to the mole fraction of the molecules of the first type.

Collisions per mole =
$$K \times N_1 \times N_2$$
 (1a)
Collisions per liter = $K \times N_1 \times C_2 = K \times \Sigma C \times N_1 \times N_2 = K/\Sigma C \times C_1 \times C_2$ (1b)

The kinetic theory assumes that the speed of a bimolecular reaction is proportional to the number of collisions between reactive molecules of each sort. In an ideal solution, where the fraction of the molecules which are reactive is constant, the speed is proportional to the number of collisions between all the molecules. Using the two values of speed defined above, and recalling that in an ideal solution activity is proportional to mole fraction

$$-dN_1/dt = K' \times N_1 \times N_2 = K'' \times a_1 \times a_2$$
(2a)
$$-dC_1/dt = K' \times \Sigma C \times N_1 \times N_2 = K'/\Sigma C \times C_1 \times C_2 = K'' \times \Sigma C \times a_1 \times a_2$$
(2b)

The general equations are obvious. If m represents the number of molecules of each kind which react, they are

$$-dN_1/dt = K'' \times a_1^{m_1} \times a_2^{m_2} \times \dots \times a_n^{m_n}$$
(3a)
$$-dC_1/dt = K'' \times \Sigma C \times a_1^{m_1} \times a_2^{m_2} \times \dots \times a_n^{m_n}$$
(3b)

This derivation holds only for ideal solutions, but it does show that, if its logic is correct, the term s for ideal solutions when the equation is written in terms of activities is the quantity transformed in unit time per single mole of all components.

For the purpose of integration, the activities which change during the course of the action must be expressed in the same units as the differential. For an apparently unimolecular reaction⁵ the ΣC 's cancel in the second form, and the value of K is the same whether the speed is expressed in terms of mole fractions or of concentrations. In general $K_C = K_N(\Sigma C)^{1-n}$ where n is the apparent order of the reaction. A dilute solution, as ordinarily considered, is one in which ΣC is constant and independent of the composition. For such a solution K_C is proportional to K_N for a reaction of any order.

To extend this treatment to semi-ideal solutions, in which all the deviation from ideality is due to chemical action, it is necessary and sufficient to express the mole fraction of each reactant as it exists in solution and not as moles added.

The extension to solutions in general must be made by analogy, but it is rendered more probable by the fact that most solutions do not deviate much from semi-ideality. At present we cannot apply the theory of the speed of reaction unless the activity of each reactant whose concentration changes during the course of the reaction is proportional to its mole fraction: so the extension need not be too general. We know that in a reversible reaction near equilibrium the speed of each of the two opposing reactions must be proportional to the activities of the reactants, regardless of the nature of the environment. From the above argument it is evident that the reaction speed is proportional to the activities of the reactants in any reaction in ideal or semi-ideal solutions. The only generalization which will include both these special cases is that the speed of all reactions is proportional to the activities of the reactants: that Equations 3a and 3b hold for all reactions. This is further justified by the conclusion that the activity contains factors for both the proportion of reactive molecules and the frequency of collision.

This interpretation of activity offers an explanation of the conclusions of Brönsted² concerning the salt effect on the speed of reactions, particularly between ions. Brönsted considers that every reaction takes place by the formation of an intermediate complex of extreme instability, whose activ-

⁵ The order of a reaction is the number of molecules that react according to the equation; the apparent order is the number of those whose activity changes.

ity corresponds to its electrical charge which must equal the algebraic sum of the charges of the reactants. The speed of reaction is proportional to the activities of the reactants and inversely proportional to the activity coefficient (a/C) of this critical complex.

The formation of a complex which reacts immediately is synonymous with reaction on collision. The salt effect on reaction speed might be due to a change in the proportion of reactive molecules or to a change in the collision frequency. The effect on the activity coefficient might be due to either of these same causes. The fact that these effects depend only on the ionic type indicates that it is the latter which is changed, for the fraction of the ions which are already active must vary greatly for ions of the same valence type. Both salt effects are probably due to a change in the medium which alters the effect of the electrical charges upon each other, the nature of which is such that, when the frequency of collisions between oppositely charged ions is increased, that between similarly charged ions is decreased, and vice versa. Since the effect on the speed of reaction is due to the same cause as that on the activity, it should be inversely proportional to the activity coefficient of the complex formed during collision. This factor represents a true catalytic action in the salt effect, distinct from and superposed on the change in activities of the reactants.

Brönsted's conclusions are based on results with solutions 0.1 N or more dilute, which may be considered as dilute solutions by the definition given above; in such solutions the activity coefficients are approximately equal for ions of the same valence type. To apply this theory to concentrated solutions, the activity coefficient of the complex should be defined as the activity divided by the mole fraction: $f_C = a_C/N_C$. Moreover, in concentrated solutions the activity coefficient is not the same for all ions of the same valence type. Since the activity coefficient of an extremely unstable substance can never be measured directly, this introduces a new source of uncertainty into the study of concentrated solutions. In ideal or semi-ideal solutions f_C is a constant. The general equations become

$$-dN_1/dt = K''/f_C \times a_1^{m_1} \times a_2^{m_2} \times \dots \times a_n^{m_n}$$

$$-dC_1/dt = K''/f_C \times \Sigma C \times a_1^{m_1} \times a_2^{m_2} \times \dots \times a_n^{m_n}$$
(4a)
(4b)

Viscosity and Speed of Reaction

Those who have assumed that the viscosity of a medium affects the reaction speed have generally assumed also that the speed of any reaction is inversely proportional to the viscosity, which seems to imply that the viscosity is a symptom of an inertia in the medium which affects anything happening in it. Others^{6,7} have maintained that the effect of viscosity is at most very much smaller than that calculated by this assumption.

⁶ Arrhenius, Z. physik. Chem., 28, 317 (1899).

⁷ von Halban, *ibid.*, **67**, 129 (1909).

Moran and Lewis³ consider that the frequency of collision is a function of the viscosity, and that it is only through influencing this frequency that the viscosity affects the reaction speed. Then the viscosity should have no effect on a unimolecular reaction. In the case of the reaction of sucrose with hydrogen ion, the heavier sucrose molecule moves so much more slowly that it may be considered as motionless, and the effect of viscosity on the reaction speed is proportional to its effect on the mobility of hydrogen ion as measured by conductivity: it is approximately inversely proportional to the square root of the viscosity.

I believe that the speed of reaction is independent of the viscosity. My conception of the influence of viscosity is essentially that of Arrhenius, 6 which deserves restatement and emphasis and requires some minor modifications. Since the influence of a substance on the viscosity of a medium depends largely upon the size of its molecule, we will simplify the discussion by neglecting other factors and defining size as effect on viscosity.

Conductivity is not proportional to fluidity (the reciprocal of viscosity) but to some fractional exponent of it. The usual explanation of this smaller exponent is that the ions are too small to obey Stokes's law and that, when the individual molecules are considered, a solution is heterogeneous. The fluidity measures the mobility of all the molecules, large and small, while the conductivity measures the mobility of the smaller ions past the larger molecules. The effect of the larger molecules on the average mobility, when they themselves take part in the motion, is greater than their blocking effect upon smaller molecules or ions. 8,9,3

To extend this reasoning to the speed of reaction we must consider that both fluidity and conductivity depend upon the ordered motion of migration. Both are measured by the linear velocity over distances very large compared to the free path of the molecules. The speed of reaction, on the other hand, depends upon the frequency of collision and, therefore, upon the chaotic motion of thermal agitation. Although the free path in liquids is extremely small, an ion, when the direction of its motion is changed by collision, has exactly the same probability of colliding with a reactive molecule as though it had continued its motion in the original direction.

According to the theory of the equipartition of energy and the kinetic molecular concept of temperature, the speed of thermal motion is a function only of the temperature, and is independent of the viscosity or any other property of the medium. In fact, the kinetic explanation of viscosity considers that viscous resistance is exerted by means of the change of energy of ordered linear motion to that of chaotic thermal

⁸ Green, J. Chem. Soc., 93, 2049 (1908).

⁹ MacInnes, This Journal, 43, 1217 (1921).

agitation. Since the frequency of collision and the speed of reaction depend only on this latter type of motion they cannot be influenced by viscosity.

The experimental study of the effect of viscosity on reaction speed is inconclusive because of the failure to eliminate other factors. The viscosity of a medium cannot be changed without changing the medium, which may also change the activity coefficient of any reactant or the specific catalytic effect of the medium. The effect on activity coefficients may be determined by measuring the activities, and that on the catalytic effect only by measuring the speed of several reactions in the same media. The fact that viscosity and speed of reaction change together cannot show how the two are related, or even that they are related.

Very dilute solutions of agar-agar or of gelatin have very great viscosities, while the effect of these solutes on other properties is small. It has been found that the speed of hydrolysis of methyl acetate by hydrochloric acid in such solutions, even when set to a jelly, is almost as great as in water. ^{10,11} The small change can probably be accounted for by a change in the activity of the hydrogen ion. This eliminates the possibility of a general inertia due to viscosity. It cannot decide between the two other theories, for the conductivity and diffusion are also nearly the same in these jellies as in water.

Arrhenius⁶ believed that the fact that non-electrolytes have a very small effect on the speed of sucrose inversion compared to their effect on viscosity¹² proves that the reaction speed is very nearly independent of viscosity. But there may be a compensating increase in the activity of one of the reactants; witness the effect of sucrose itself on the hydrogenion activity.

The same objection applies to the measurements of reaction speed in water-alcohol mixtures.¹³ There must be a great change in the activity coefficients of most substances as the solvent changes, for the solubilities change greatly. The activity coefficients of ions apparently change also. The measurements of Pearce and Hart,¹⁴ calculated for 0.1 mole in a liter of solvent, show that the mean activity of lithium and chloride ions is 5 times as great in methyl alcohol, and 8 times in ethyl alcohol, as in water; but no activities have been measured in connection with the speed of reaction measurements. Moreover, although the viscosities of mixtures of water-alcohol pass through a maximum, the speed of re-

¹⁰ Reformatsky, Z. physik. Chem., 7, 34 (1891).

¹¹ Callow, Trans. Faraday Soc., 11, 55 (1915).

¹² Arrhenius, Z. physik. Chem., 4, 226 (1889).

¹³ This objection applies also, as regards the activity of the acid, to the work of W. H. Garrett and W. C. M. Lewis [This Journal, 45, 1091 (1923)] on the formation of valerolactone in solutions containing sucrose.

¹⁴ Pearce and Hart, This Journal, 44, 2411 (1922).

action sometimes increases, sometimes decreases, and sometimes passes through a minimum, which does not, however, correspond to the viscosity maximum.¹⁵

Particularly interesting are the results of Kistiakowsky on the reaction of formic acid with ethyl alcohol and that of ethyl formate with water. When the reactions are catalyzed with hydrochloric acid the speeds of both decrease slowly as water is displaced by alcohol to a minimum at about 60% alcohol, and then increase rapidly. Without a catalyst both decrease much more rapidly and continuously to 90% alcohol. The difference in the reactions with and without catalyst is very possibly a measure of the hydrogen-ion activity.

The only measurements in which all the activities have been measured are those of Buchböck16 on the hydrolysis of carbonyl sulfide in aqueous solutions of various salts and acids, published soon after the first suggestion of the activity theory, under the name of solubility theory, by Van't Hoff. 17 Probably the speed of this reaction should not be affected by the viscosity according to any kinetic theory of viscosity, since the reaction is unimolecular or with the solvent which is in large excess. The constants quoted do show that, corrected or not by multiplying by any power of the viscosity, the concentration theory, the simple activity theory, and the unmodified theory of Brönsted all fail to give constants. The modified theory of Brönsted explains the results if the speed is independent of the viscosity and the activity coefficient of the critical complex increases linearly with some function such as the "ionic strength" of Lewis and Randall. 18 The concentrations of the ions may be estimated roughly from the molality of the solution necessary to give the same freezing-point depression as does N hydrochloric acid.

The Inversion of Sucrose

Most of the assumptions necessary to the application of this theory to the inversion of sucrose were discussed in my previous paper,⁴ but some require reconsideration in the light of new work. The numbers following the subtitles refer to the pages of the previous paper.

Activity of Sucrose (2391-2, 2399-402).—There seems no reason to change the conclusions that the reaction is unimolecular with respect to

Walker and Kay, J. Chem. Soc., 71, 489 (1897). Kistiakowsky, Z. physik. Chem.
 27, 250 (1898). Caldwell, Proc. Roy. Soc., 78A, 272 (1906). Acree, Am. Chem. J., 41, 457 (1909). Reid, ibid., 41, 483 (1909). Schilow and Pudovkin, Z. Elektrochem., 16, 125 (1910). Burrows and Fawsitt, J. Chem. Soc., 105, 609 (1914). Burrows, ibid., 105, 1260 (1914).

¹⁶ G. Buchböck, Z. physik. Chem., 34, 229 (1900).

¹⁷ Van't Hoff, "Lectures on Theoretical and Physical Chemistry," Eng. ed., 1898, Part I, pp. 217 ff.

¹⁸ Lewis and Randall, This Journal, 43, 1112 (1921).

sucrose, and that the activity of sucrose is proportional to its mole fraction.¹⁹

Constancy of k (2391–2, 2399–402).—Fales and Morrell²⁰ claim that k, the constant for a unimolecular reaction, is not always constant during the course of a single reaction. Unfortunately, their experiments were not carried out in duplicate, and it is difficult to determine what part of their variation should be attributed to a real lack of constancy and what part to experimental error. The more complete details in Morrell's dissertation indicate two types of variation from constancy.

The first is abnormally high values of k for the first 1 or 2 minutes. This is noticeable only in the $0.1\ N$ or more concentrated solutions, for in the more dilute solutions the total change in so short a time is negligible. The abnormality is irregular and bears no apparent relation to the acid or sugar concentration. Two probable causes are: (1) an error in the measurement of time, which is unavoidable when the time interval is not great compared to the time of delivery of the pipets; and (2) an increase in temperature for the first few minutes due to the heats of dilution. Fales and Morrell have discarded these abnormally high values in calculating their average constants. They probably do not indicate a real abnormally high initial speed.

The second is a gradual increase of the reaction speed, which appears only in the solutions more concentrated in hydrochloric acid than $0.3\ N$. Their solutions of $0.3\ N$ acid have about the same hydrogen-ion activity as the upper limit in the solutions studied by Lewis. 21,3 We are, therefore, justified in assuming that such an increase does not exist in these solutions. Moreover, such a gradual variation would appear in their method. 22

Activity of Water (2392-6).—The activity of the water cannot be determined directly, since it changes materially during the course of inversion. It is determined from the activity in solutions without acid, and corrected for the effect of the acid by two assumptions which seem to give the minimum and maximum probable values. For $0.1\ N$ sulfuric acid the greatest correction is 0.6% and the greatest difference between the two assumptions is 0.4%; for $0.1\ N$ hydrochloric acid the corresponding values

¹⁹ In their statement that this question involves a difficulty to which attention had not hitherto been drawn, Moran and Lewis³ apparently overlook the discussion in my previous paper referred to above.

²⁰ Fales and Morrell, This Journal, 44, 2071 (1922). Morrell, Dissertation, Columbia University, 1921.

²¹ Jones and Lewis, J. Chem. Soc., 117, 1120 (1920).

²² The agreement between the results of Moran and Lewis and of Fales and Morrell noted by Lewis, Merriman and Moran [This Journal, 45, 711 (1923)] does not depend on the form of constant used by the authors, but arises through agreement of the two observations in both k and $a_{\rm H}+$.

are twice as great. The two assumptions lead to practically the same conclusions as to the number of water molecules taking part in the reaction.

Activity of Hydrogen Ion (2392).—It was previously assumed that the hydrogen electrode with saturated potassium chloride bridge gave an accurate measure of the hydrogen-ion activity. The discussion in another paper²³ indicates that this cannot be true with varying acid concentration, but that it is probably true with varying sucrose concentration. However, this must be recognized as an assumption with some theoretical justification. Without it, the measurements of sucrose inversion are worthless as a test of theories of the mechanism of reaction.

Fales and Morrell²⁰ claim that the reaction speed is not exactly proportional to the hydrogen-ion activity with varying acid concentration. Their results can be explained by the error in the determination of the hydrogen-ion activity and by the theory of Brönsted.

Activity Coefficient of Critical Complex.—If Equations 4a and 4b are correct, the activity coefficient of the critical complex must be taken into account, but it cannot be measured directly and cannot be assumed to be equal to that of the hydrogen ion. It was shown²³ to be probable that the two most important reasons for the change in activity coefficients are the change in the fraction of unhydrated ions and the effect of electrical charges on one another. In the case of a critical complex the first is already taken into account in the activities of the reactants. With varying sucrose concentration the total ionic concentration is probably unchanged, so we will assume that the activity coefficient of the critical complex is constant. This assumption has about the same degree of substantiation as the one that the saturated potassium chloride bridge gives constant liquid-junction potentials with these solutions.

For varying acid concentration the best we can do is to assume that the activity coefficient of the critical complex is the same as that of the potassium and chloride ions, which appear not to be greatly affected by varying water activity but to depend on the changing concentration of ionic charges. Frankly discarding the experimental determinations of hydrogenion activity, and taking the activities of hydrogen ion and of chloride ion in the dilute sucrose solutions as the same as in water solutions of the same molality, we find for the results of Fales and Morrell constants within the variation of their two series from each other, except for the 0.001 N solutions, where the concentration of acid may well be reduced by some side reaction.²⁴ It is not worth while publishing the details with so many approximate assumptions involved.

²³ Scatchard, This Journal, 45, 1716 (1923).

²⁴ A similar treatment of the results of Harned and Pfanstiel [This Journal, 44, 2193 (1922)] on ester hydrolysis gives less constant values than those quoted and explained in their article. This may be due to the uncertainty about the activity of the ester and about the number of water molecules which enter into the reaction.

Equation for Sucrose Inversion.—It is convenient to collect here the definitions of the various symbols.

N= mole fraction; C= concentration in moles per liter; $\Sigma C=$ total moles of all components per liter; a= activity, on a scale such that it is unity for pure water or for solutions without sucrose; f=a/N; $\eta=$ viscosity; x=0.52 at 20° and 25°, 0.55 at 35° and 40°; n= an integer (trial values = 5, 6, 7); subscript wapplies to water, H to hydrogen ion, S to sucrose, and S to the critical complex; S = S to Moran and Lewis.

Since the reaction is unimolecular with respect to sucrose and hydrogen ion and the activity of the sucrose is the only one that changes enough to need consideration, Equation 4b becomes;

$$-dC_{S}/dt = K''/f_{C} \times \Sigma C \times a_{S} \times a_{H} \times a_{W}^{n} = K''/f_{C} \times \Sigma C \times 1/\Sigma C \times f_{S} \times C_{S} \times a_{H} \times a_{W}^{n}$$

$$K'' = f_{C}/(f_{S} \times a_{H} \times a_{W}^{n}).1/C_{S}.dC_{S}/dt = f_{C}/(f_{S} \times a_{H} \times a_{W}^{n}).k$$
(5)

We have assumed that $f_{\mathbb{C}}$ and $f_{\mathbb{S}}$ are constant; by Brönsted's theory we might make the less sweeping assumption that their ratio is constant. By the simple activity theory $f_{\mathbb{C}}$ should be replaced by 1. In any case the ratio may be incorporated in the constant, and we reach a result identical with that of the previous paper.

$$K_{\rm S} = \frac{k}{a_{\rm H} \times a_{\rm W}^n} \tag{6}$$

Other Constants.—Lewis and his co-workers have proposed two constants for this action, which we will designate by the initials of the authors.

$$K_{\rm J+L} = \frac{k}{a_{\rm H} \times C_{\rm W}} \qquad (7) \qquad K_{\rm M+L} = \frac{k \times (C_{\rm W} - 4C_{\rm S}) \times a_{\rm W}^2 \times \eta^2}{a_{\rm H}} \qquad (8)$$

 K_{J+L} differs from K_S only in the replacement of the activity of water by its concentration. It depends upon all the assumptions mentioned above except those concerning the activity of water. It must be rejected, however, unless the activity theory is correct for some substances but not for others.

 $K_{\rm M+L}$ differs in the definition of reaction speed and in assuming that the speed is inversely proportional to η^x . For these solutions $(C_{\rm W}-4C_{\rm S})$ is approximately equal to $a_{\rm w}^{10}$, and η^x to $a_{\rm w}^{-18}$, when all are expressed on such a scale that they are unity for pure water. Then the insertion of these terms makes a difference corresponding to + 10 and - 18, respectively, molecules of water reacting with each molecule of sucrose. Obviously, no conclusions can be drawn regarding the mechanism of the reaction until both of these two factors are settled. $K_{\rm M+L}$ depends upon all the other assumptions that does $K_{\rm S}$.

Experimental Results.—The work of Moran and Lewis with hydrochloric acid as catalyst offers another check of the theory. In calculating the activity of water its activity in $0.1\ N$ hydrochloric acid is taken as 0.9965 (determined from freezing-point measurements). $K_{\rm J+L}$ is 55.55 times as great as the value given in the formula. The values of $K_{\rm M+L}$

are taken directly from the paper of Moran and Lewis and also differ from the value given by the formula by a constant factor, different for each temperature. These differences arise from different units for activities and concentrations, but they can make no difference for a comparison of relative values.

Table I Speed Constants by Various Formulas

SPEED CONSTANTS BY VARIOUS FORMULAS												
—First assumption——Second assumption—												
Conc.	$K \times 10^{6}$	ир	Mα	$K_{\rm S} \times 10^{\rm s}$ $n = 15$	$K_{\rm S} \times 10^{\rm s}$ $n = 6$	$K_{\rm S} \times 10^5$ $n = 7$	Mø	$K_{\rm S} \times 10^5$ $n = 5$	$K_{\rm S} \times 10^5$ $n = 6$	$K_{\rm S} \times 10^5$ $n = 7$	$K_{ m J+L} imes 10^5$	KM+L×105
						At 2	25°					
0.0	(1.21)	1.00	0.997	(1.23)	(1.23)	(1.24)	0.997	(1.23)	(1.23)	(1.24)	(1.21)	(1.31)
10.0	1.36	1.20	.991	1.19	1.20	1.21	. 990	1.19	1.20	1.22	1.21	1.28
20.0	1.52	1.44	.984	1.14	1.16	1.18	. 982	1.16	1.18	1.20	1.21	1.25
30.0	1.68	1.74	.976	1.09	1.12	1.14	.973	1.11	1.14	1.17	1.19	1.24
40.0	1.83	2.09	.965	1.05	1.08	1.12	. 961	1.07	1.11	1.16	1.17	1.24
50.0	1.99	2.50	. 952	1.02	1.07	1.12	.947	1.05	1.10	1.17	1.16	1.24
60.0	2.15	3.00	.934	1.01	1.08	1.16	.928	1.04	1.12	1.21	1.15	1.27
70.0	2.30	3.60	.911	1.02	1.12	1.23	. 903	1.06	1.18	1.30	1.15	1.28
Av.				1.07	1.12	1.17		1.10	1.15	1.20	1.18	1.26
						At 3	35°					
0.0	(5.00)	1.00	0.997	(5.08)	(5.09)	(5.11)	0.997	(5.08)	(5.09)	(5.11)	(5.00)	(12.5)
10.0	5.65	1.19	.991	4.97	5.01	5.06	.990	4.99	5.04	5.09	5.08	12.4
20.0	6.33	1.42	.984	4.83	4.91	4.99	. 983	4.86	4.94	5.03	5.11	12.3
30.0	7.00	1.71	.976	4.62	4.74	4.85	. 973	4.69	4.82	4.96	5.05	12.2
40.0	7.66	2.05	.965	4.47	4.63	4.80	.962	4.54	4.71	4.90	4.99	12.2
50.0	8.33	2.45	.952	4.33	4.55	4.78	.947	4.45	4.69	4.96	4.94	12.1
60.0		2.95	.935	4.30	4.60	4.92		4.47	4.81	5.19	4.94	12.5
70.0	9.66	3.53	.912	4.34	4.76	5.21	.904	4.53	5.01	5.55	4.91	12.3
Av.				4.55	4.74	4.94		4.65	4.86	5.10	5.00	12.3

TABLE II

ROOT-MEAN-S	QUA	re Deviat	ions Divi	DED BY AVI	RAGE -	
Formula	n	H ₂ SO ₄ 20°	H ₂ SO ₄ 40°	HC1 25°	HC1 35°	Av.
	5	0.033	0.057	0.060	0.054	0.051
Ks First assumption	6	.014	.039	.040	.033	.031
	7	.031	.038	.034	029	.033
	5	.028	.051	.048	.041	.042
$K_{\mathbf{B}}$ Second assumption.	6	.016	.036	.032	.027	.028
	7	.038	.042	.037	.040	.039
K_{J+L}		.018	.024	.021	.014	.019
K _{M+L}		.031	.036	.014	.010	.023

The values of the constants are given in Table I. Table II contains the relative root-mean-square deviations of the experimental values from their averages for both $0.1\ N$ sulfuric and hydrochloric acids, and the last column gives the average of the 4 series. These values are equal, within 1%, to the relative probable error of a single determination, and offer the simplest means of comparing the constancy of the constants.

Examining first the application of my formula to the inversion catalyzed

by hydrochloric acid, it is evident that the constancy is not so good as with sulfuric acid and that all the results show a minimum for medium concentrations. Remembering that the second assumption for determining $a_{\mathbf{w}}$ is more probable than the first, we see that these results confirm those with sulfuric acid in indicating that n is 6, although the possibility that it is 7 is not eliminated.

To compare the three formulas we will take $K_{\rm S}$ for the second assumption with n equal to 6. Of the three formulas, $K_{\rm J+L}$ fits the experimental data best, in spite of the fact that $K_{\rm S}$ contains an arbitrary integer and $K_{\rm M+L}$ an arbitrary non-integral constant, both chosen to give the best agreement with experimental data. The difference between the latter two is small and may be accounted for by the greater flexibility of the arbitrary constant in $K_{\rm M+L}$. It is doubtful if any of the variations exceed the sum of the experimental errors. The experimental results certainly cannot serve as a criterion to choose between the several formulas; this choice must be based on the accuracy and reasonableness of their assumptions. Only after the formula is established can the experiments determine the number of water molecules which react with one molecule of sucrose.

The Hydration of Sucrose.—Moran and Lewis find confirmation of their formula from their conclusion that osmotic-pressure measurements prove that sucrose exists in water solution entirely as a tetrahydrate. I have already discussed the accuracy of the various methods of determining the extent of hydration, the fact that all methods point to decreasing hydrate formation with increasing concentration, and that the most accurate results (from vapor pressures) are best accounted for by the formation of a hexahydrate in accordance with the law of mass action.

The Critical Increment.—Moran and Lewis claim further confirmation of their theory from the fact that it gives probable values of the critical increment, that is values which agree with Lewis's radiation theory. The critical increment is a function of the fraction of reactive molecules. The activity must be a function of the same quantity, whether the nature of that function is correctly derived above or not. It follows that the critical increment cannot be derived from the reaction speed in terms of activities, but must be in terms of concentrations or mole fractions. Since the volume changes very little with the temperature, the difference between these last two is negligible. A detailed discussion of this complicated question is out of place here, but the critical increment, calculated from concentrations or mole fractions, is practically the same for the two theories of the reaction mechanism.

Summary

1. A kinetic interpretation of activity is given which justifies the expression of reaction speed in terms of activities and which demands that the

25 Scatchard, This Journal, 43, 2406 (1921).

speed so expressed be defined as moles transformed in 1 mole of all components.

- 2. This interpretation offers a possible explanation of the salt effect on reaction speed. The expression of Brönsted must be modified for concentrated solutions.
- 3. An analysis of experimental work shows that it is of little value for determining the relation of reaction speed to viscosity. The kinetic theory, however, demands that reaction speed be independent of viscosity.
- 4. These conclusions lead to the formula for the inversion of sucrose previously presented when the concentration of electrolyte is unchanged.
- 5. The experimental measurements cannot serve as a criterion for choice between the various theories of the mechanism of the reaction, for the difference in agreement between the formulas is too small.
- 6. Any interpretation of the experiments depends upon the assumption that the liquid-junction potential with saturated potassium chloride is independent of the sucrose concentration.
- 7. Interpreted by the formula previously presented, the speed of inversion catalyzed by hydrochloric acid adds confirmation that 6 molecules of water react with each molecule of sucrose. The agreement is not quite so good as with sulfuric acid.

AMHERST, MASSACHUSETTS

[Contribution from the Kent Chemical Laboratory of the University of Chicago]

THE SEPARATION OF ISOTOPES. APPLICATION OF SYSTEMATIC FRACTIONATION TO MERCURY IN A HIGH-SPEED EVAPORATION-DIFFUSION APPARATUS

By Robert S. Mulliken¹

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Introduction

Important Factors for Rapid Operation of Diffusion Methods.—In the separation of isotopes, the small separating power of the diffusion methods (including evaporation) must be compensated by very rapid operation, if large separations are to be obtained in a reasonable time. The apparatus described below was designed to accomplish this object for mercury. In the course of the work, systematic fractionation as applied to diffusion methods has been rather thoroughly studied.

The most important factors for maximum speed of separation fall into two classes: those of operating speed and those of operating efficiency.²

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² By the efficiency of any given operation is meant the ratio of actual separation to the separation obtained under *ideal* conditions. The separation obtainable under ideal conditions by a process either of evaporation or of molecular diffusion, is given by Equations 7, 16 and 19 of a previous paper [(a) Mulliken, This Journal, 44, 1034 (1922)].

These two factors are usually opposed so that a compromise has to be sought. It will be shown later under "Systematic Fractionation" that about the best compromise is obtained, for the present apparatus,³ at such a rate of output D and efficiency E that E^4D is a maximum.

The total rate of output is obviously proportional to the number of operating units, and to the output of each unit. For molecular diffusion the latter is proportional, other things being equal, to the diffusion area and to the permeability of the diffusion membrane. High permeability goes with minimum thickness. In the present apparatus filter paper is used to give maximum permeability.

Efficiency is needed both in each individual operation and in the mode of division and combination of fractions in systematic fractionation. Efficiency of the individual operation depends on the design of the units. The same effect as that of increased efficiency is secured when two different methods of separation can be combined as successive steps in one operation. This principle is used in the present apparatus by the superposition of an efficient molecular diffusion on an inefficient evaporation. Closely related to the efficiency factor is the variation from one element to another, or especially among compounds of a single element, in the degree of separation obtainable in a given operation. The element mercury here used is decidedly unfavorable from this point of view, but is unusually good from the points of view of practicable speed of turn-over, and of general convenience of handling.

Description of Apparatus in Present Form

In the following paragraphs the apparatus as now set up, its operation, and the results obtained will be described. In a later section the subject of systematic fractionation will be discussed.

The method consists essentially in systematically repeated operations in each of which mercury vapor at low pressure (probably about 5 mm.), generated under such conditions that a partial separation of isotopes occurs, is diffused molecularly, giving a further separation. The chief advantage of the method is the relatively very high speed at which it can be operated without great sacrifice of efficiency, combined with the facts that the apparatus requires only tap water for perfect cooling, and that a high vacuum is not needed.

Vacuum System.—The apparatus consists of 6 similar upright units used independently but in cooperation. They are set up on a table and

³ In general, maximum E^3D is a more appropriate criterion.

⁴ See table of separation coefficients, Mulliken and Harkins, This Journal, 44, 55 (1922).

⁵ A set of connected units was at first considered, but was rejected for several reasons, one of which is that in such a set the evaporation effect would be nullified, as far as separation of isotopes is concerned:

each is connected through a 3-way stopcock to 2 vacuum lines, evacuated by a Cenco Hyvac pump. A McLeod gage is used to read the pressure. The units are ordinarily all connected to the same line. Any unit that needs to be repaired or emptied is switched to the other line, and air is admitted. To bring such a unit again into operation, the second line is opened to the pump and the first line shut off. As soon as the unit is evacuated, it is switched to the first line with the other units, and all are again connected to the pump. Several stopcocks are used to make these operations possible. Little trouble was experienced from leakage, especially since an air pressure of 0.2 mm. is as good as the highest vacuum, and even 0.5 mm.

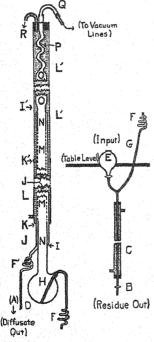


Fig. 1.—Section of type I unit

lowers the efficiency only slightly. There is little or no leakage in the units themselves, so that they can be shut off from the pump for considerable periods.

Design of Units.—The best design for the individual units, as now worked out, is shown in Fig. 1. They are made entirely of Pyrex glass.

In the operation of the apparatus the mercury is evaporated from the 500cc. flask H. A dirty evaporating surface improves the efficiency, as noted in a previous paper.6 The mercury is fed into the evacuated flask from the 100cc, funnel E through the capillary tube G, the highest point of G being about 34 cm. above the stopcock on E. The inner end of tube G touches the bottom of the flask H, so that at the end of a run the entire residue in the flask can be removed except for a few drops. To remove the residue it is necessary to admit into the flask sufficient air pressure to drive the mercury over the highest point in G.7 This is considerably more than 760 mm. above the exit stopcock B, so that a vacuum is automatically produced in the upper part of G if the mercury stops flowing. The flow of cold water in C completely cools the hot mercury on the way out.

The neck N of the flask H is sealed at I inside of a 40 mm. tube J, which is sealed in turn at K inside the 50mm. condenser jacket L. The distance IK, about 7 cm., is required for safety in making the seal I. Cold water flows continually between J and L, leaving by way of the tube R. For purposes of construction and repair, the tube L is in two sections, L and L', which are held together at K' by a thick sealing-wax joint. The tube N is continuous with the filter-paper membrane M, which has a diameter of 30 mm.

⁶ Mulliken, This Journal, 44, 2388 (1922).

⁷ It was originally hoped that the mercury would siphon out without interruption of the vacuum, but in practice the column in G usually breaks. The use of a capillary is to reduce to a minimum the volume of mercury not in action.

and a length of one meter. Moverlaps N for a distance of about 2 cm, at each end, and is fastened with water glass. The tube M is made by rolling a long strip of filter paper (one cross seam being needed if the paper is cut from a large sheet) and sticking the edges together, with a 3mm. overlap, by means of water glass. The paper turns brown on heating where it has been wet with water glass but this does not affect its strength. A number of small pieces of cork are fastened on the surface of the paper membrane to prevent it from coming into contact with the condenser wall.

Mercury vapor flows rapidly through N and M. Part of it diffuses through M, is condensed on the inner walls of J, and gathers into drops which collect in the exit from the inclined seal I. As soon as the height of the mercury in the 3mm. tube F exceeds 760 mm. the mercury flows when A is opened. The coils F reduce danger of breakage, but are perhaps unnecessary; they increase the volume of mercury not in action. The vapor which does not diffuse through M is directly exposed to condensation above I in the 20cm residue condenser O, and falls back into the flask through the stream of rising vapor. The coil P, 15 cm. long, is necessary to complete the condensation, because of the rapid upward motion of the vapor. 10

⁸ Preliminary experiments showed that the rate of diffusion is, for a given evaporation rate, directly proportional to about the 1.3 power of the length, and *inversely* proportional to about the 1.3 power of the diameter. Decrease in diameter or increase in length of the membrane, especially the former, involves increased pressure inside the membrane, which decreases the operating efficiency as well as the life of the membrane, so as to neutralize the value of the increased rate of production. The dimensions given in the text represent a fairly good—doubtless not the best—compromise between speed and efficiency for the paper here used (Whatman No. 5). The best dimensions depend in general on the permeability and efficiency-speed curve (compare Fig. 3) of the paper used. The use of a similar paper half as thick, and so twice as permeable, would double the rate of production. Resistance to heat is an all-important consideration in the choice of paper; that here used was the best of several in that respect, although not the most permeable.

⁹ It was thought that the efficiency could be improved by avoidance of this contact of the diffusion residue with undiffused vapor of different composition. Accordingly, a

type of unit (Type 2) was constructed in which I was made with an annular catch, as shown in Fig. 2, by means of which the diffusion residue was led outside the unit on its way back to the flask. (Samples of the diffusion residue could be removed through suitably placed stopcocks, so that the fraction of vapor diffusing, as well as the separate efficiencies of the diffusion and evaporation processes, could be determined; this could not be done with the Type I unit.) As will be seen from Fig. 3, this type of unit gave a lower efficiency than the simpler Type I unit, except at low rates of evaporation. The most probable explanation of this result is that the falling drops of diffusion residue obtained in Type I units serve a useful function by slowing down and mixing the central core of the rising stream of vapor with the lateral portions, thus improving the diffusion efficiency, and that this beneficial effect more than compensates the bad effect of partial establishment of equilibrium between the condensed diffusate and vapor. Both causes of inefficiency are probably always present in Type I, that of imperfect vapor mixing increasing rapidly with increase in speed of operation, and nearly disappearing at low speeds.

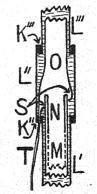


Fig. 2.—Diffusion residue catch of type II unit

10 In constructing a unit, the 96cm. outer condenser tube L is first sealed at K to the inner tube J extending from I' to I. The end I is made with a slant and the en-

The flask H rests directly on a special iron tripod with a cup-shaped piece of Nichrome wire gauze. The tripod for each unit stands in an iron pan (30 x 20 cm.) which rests on a sheet of Transite asbestos wood that extends the length of the table. To secure effective heating without causing the burner to strike back, a rather roomy asbestos hood is built over the flask and tripod, provided with an ample opening at the back for admission of air, and another near the top at the front for the exit of the burner gases. A Transite asbestos board along the front of the table keeps the heat from E, so that the next lot of material for any operation can be kept there.

The units are supported (or guided) by a single clamp placed about at K'. They are easily taken down for repair or replacement by breaking the tubes D and G, and removing the U-shaped piece Q, which is fastened in place with sealing wax. The height of the top of the unit above A and B, which are just above the floor, is about 2.8 meters.

Conditions of Operation.—The most economical evaporation rate is about 450 cc. per hour per unit. This is equal to 36 kg. per hour for the entire 6 units. The rate of diffusion in each unit is then about 70 cc. per hour. Under these conditions the efficiency of the evaporation process¹¹ is about 21%, and that of the diffusion¹² about 80%, the combined efficiency being about 96%. The combined process is outwardly completely analogous to a simple distillation having an efficiency E, which may considerably exceed 100% (but cannot exceed 200%), given by, $E = E_e + E_d((1 - F_d)/F_d) \ln(1/1 - F_d)$. Here F_d is the fraction of the generated vapor which diffuses, and E_d and E_d are the individual efficiencies (compare Ref. 2) of the evaporation and diffusion processes, respectively. 13 The curve (Fig. 3) for Type I unit trance of F is attached to it. The paper tube M is next prepared and cemented at each end to a 16cm. section of 30mm. glass tubing, closed at the outer end which later forms part of the tube N. The paper tube with its glass end-pieces is now placed inside of I. so that each end piece projects for about half its length. The seals are now made at I and I'. The operations of sealing on the section OP, and the flask H are then fairly easily accomplished. L' is attached with sealing wax at the top and bottom and the unit set up. The seals at K, I and I' require very considerable care. A distance of 6-7 cm. from I or I' to the junctions of M with N is sufficient to prevent seriously scorching the paper during the glassblowing.

¹¹ It is thought that the evaporation efficiency cannot be substantially improved at the stated speed of operation (Ref. 6).

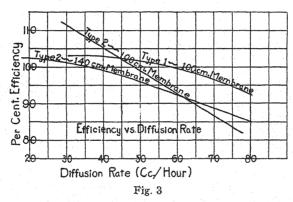
¹² The diffusion efficiency is limited by the two factors referred to in Ref. 9, and also by the fact that the interstices between the fibers of the filter paper are, except at very low rates of evaporation, relatively too large as compared with the mean free path in the vapor (compare Ref. 4 for discussion). This of course varies with the paper used. The effect of back pressure, due to the vapor pressure of mercury at the temperature of the cooling water used, is negligible in all cases.

By using an apparatus somewhat like Type II (Ref. 9), a diffusion efficiency probably approximating 100% was obtained in several of the slower runs, where the pressure of mercury vapor is estimated to have been less than 2 mm. These runs have been used as the basis for a new value of the separation coefficient. This was reported in a previous paper (Ref. 6), and is here used as the basis for all calculations of efficiency.

¹³ The adjustment of F_d is an important problem of design. Low F_d means increased E, but decreased D, and vice versa.

shows the relation of efficiency E to speed D for the present type of unit. 14

With all 6 units operating effectively and continuously, a spread of 0.10 units of atomic weight, with a set of 50cc. fractions at equal intervals of about 0.004 units between —0.05 and +0.05 could be produced in about 80 hours of diffusion. The time required for any spread (so long as complete separation of the individual isotopes is not approached) is about proportional to the cube of the difference between the atomic weights of the extreme fractions, as is shown by a study of the theoretical course of the fractionation. This will make a very slow process of obtaining a large separation, such as one unit of atomic weight. A complete set of intermediate fractions or working stock, of volume and distribution about as described above is necessary in increasing the separation of extreme fractions. Any separation can, however, be readily increased by about



0.05 units by evaporating the final extreme $50 \, \mathrm{cc.}$ fractions to $0.5 \, \mathrm{cc.}$ each in a small apparatus.

The actual number of working hours required for any separation will be about twice or thrice the time of diffusion as given above. This is due to the considerable time needed for repair and replacement of units, to loss of time when the units are not in operation together, to time required

 14 E is determined by determining the relative density of a sample of diffusate and one of residue for a run at the desired speed, and applying Equation 19 (Ref. 2). The difference in their densities is usually about 36 parts per million for 100% efficiency, and can be determined, if desired, to about 2%.

¹⁵ This corresponds to E = 0.92, and a cut (see Ref. 4) of 2 in each operation.

¹⁶ The time required for a given extreme separation is directly proportional to the size of the stock fractions. The minimum practicable size of fraction is determined chiefly by the falling off of efficiency with small volumes, and by the increased heating of the vapor and consequent effect on the life of the membrane. The loss of value by mixing during refilling also becomes increasingly important with small volumes. An improvement in the present apparatus which would permit smaller operating volumes without decrease of speed, would be most valuable.

in starting and stopping the apparatus and in emptying and refilling units, and to low efficiency in operation for various reasons. The last two factors are particularly important in the case of the light fractions; a given amount of progress takes about 50% longer for them than for the heavy fractions. To avoid loss of time by too frequent replacement of units, the diffusion rate should not be allowed to exceed about 70 cc. per hour for any considerable period (a much lower speed limit is necessary at *small volumes*; compare Ref. 19), as the life of the membrane is limited by the temperature to which it is subjected. The actual rate of progress is lowered very little if the diffusion rate falls as low as 60 cc. per hour, since the increased efficiency nearly compensates the decreased production rate, the E^4D curve being nearly flat for some distance near its maximum.

Method of Operation and Accounting System.—In filling a unit at the beginning of a run, the lightest fraction of sufficient size previously produced is introduced into the apparatus. As the diffusion proceeds, the density of the residue in the flask increases. Previously produced fractions of progressively increasing density are successively introduced at appropriate times, while the diffusate is removed in successive fractions equal in volume to about 30% of the flask contents (but compare below). The process continues until after the last of the earlier series of fractions has been introduced, and the residue in the flask has become too small for efficient operation. Air is then admitted to expel the residue through G. The unit can be emptied, re-evacuated and refilled in 30 minutes under favorable conditions. With each repetition of such a series of operations the lightest and densest fractions produced become more widely separated. At a given time the different units are in general at different states in their passage through the series.

An essential part of the operation is a method for rapidly calculating and recording the composition of each fraction as it is produced, for keeping account of the volume and composition of the material in the units, and for calculating the proper times to add more material. This last is done whenever the composition of a previously produced fraction is identical with that of the contents of a unit, except that the contents of a unit at any time is limited to 300–350 cc., or unless it is desired to reduce the volume of the contents before emptying a unit and starting on the retreatment of a lighter fraction. A pad of record sheets is kept on a

¹⁷ Efficiency is lost (1) by mixing of partly separated fractions (a) whenever the diffusion rate changes suddenly, as when the air pressure suddenly rises, (b) in the normal procedure of combining fractions on the shelves if they differ by less than 6 parts per million, (c) whenever a unit is emptied and refilled (about 2 cc. of diffusate and diffusion residue remains on condenser walls, etc., and a little in the flask); (2) when the volume in the flask is less than 150 cc. (See Ref. 19). Effects 1c and 2 influence the light more often than the heavy fractions.

¹⁸ The reconstruction of a unit with a new membrane takes about 20 hours.

small shelf projecting from the front of each unit, and on this the "credits." "debits" and "balance," both volume and composition, are recorded. For rapid calculation of the composition of any diffused fraction, a table has been prepared showing the decrease in density of the diffusate over a range of efficiency of 72-110%, and over a range of the fraction of the balance diffused of 0-62%. In order to determine the composition of a given diffused fraction its volume is measured and divided by that of the previous balance to give the proportion diffused; the diffusion rate is calculated from the time, and the efficiency is then read from a previously determined plot (like those in Fig. 3) of efficiency against speed for that unit;19 the density change (decrease) is recorded, and to it is added the composition figure (expressed as parts per million of density greater or less than that of ordinary mercury); the product is then transferred to a properly labeled bottle on a storage shelf. The change of density of the residue is read from another chart on which efficiency is plotted against diffused fraction, and the density and volume of the residue (balance) in the flask are recorded. The volume and density of the fraction newly added are at the same time recorded, together with the resulting new balance. The volume which must diffuse, in order to bring the contents of the flask to the composition of the next lightest fraction on the storage shelf, is then calculated, and diffusion allowed to proceed to this point, when the fraction in question is added, the diffusate removed, and the calculations described above are repeated. To avoid indefinite subdivision of fractions, any two fractions on the shelves differing by 6 parts per million or less are combined to give a single fraction. This means no great loss since the value of a separation between two fractions is proportional to the square of that separation (see Systematic Fractionation), and since a separation of about 35 p. p. m. between diffusate and residue is produced in normal operation. Similarly there is no great loss in value (only 1.3%) in the collection together of diffused fractions totaling as much as 30% of

¹⁹ The efficiency curve should be the same for all units of the same type. If the curve for that type has been determined, it is necessary only to determine 2 or 3 points for each new unit, to make certain that the unit has no defect or unusual characteristic. This can be done rapidly by comparing the densities of a diffusate and residue for each of 2 or 3 rates of diffusion. It is also necessary to check occasionally the results obtained with each unit to make sure that it is still in good condition.

The efficiency of a unit at any speed is lower, and the vapor temperature much higher, when the flask contains less than 100 cc.; the efficiency drop is roughly 2% at 100 cc. and 5% at 50 cc. Low volumes occur mostly with fractions near the extremes, thus increasing difficulties there.

High pressure (more than about 0.5 mm.) increases the fraction which diffuses. The loss in efficiency under such conditions is about the same as if the increased diffusion rate were due to an increase in the evaporation rate. (High pressure may be caused by air admitted accidentally through the stopcock below E, after a fraction has been added, or by breakage or leakage in the apparatus, etc.)

the previous balance (cut = 10/7), although the first and last portions of such a fraction differ in density by 10 p. p. m. The corresponding figures for a 50% fraction (cut of 2) are 4.0% loss, and 22 p. p. m. A great number of very small fractions would require an impossible amount of attention from the operator. The number of fractions removed per hour, at 70 cc. per hour per unit, is 6×70 divided by Q_d , or $420/Q_d$, where Q_d is the average size of the fractions as removed. The work of taking 10 fractions per hour, inspection of the apparatus, and occasionally emptying and refilling a unit, is enough to keep one man busy. When a unit is refilled, allowance has to be made, in recording the composition of the first fraction added, for the fact that about 2 cc. of the previous contents still remains in the units, chiefly adhering to the condenser walls.

Except in the early stages of operation, the best method is, all things considered, to make a series of cuts of 2, that is, diffusion of 50% of the flask contents between refillings. The changes of composition are thus equal and opposite for the two fractions produced in each stage of the operation. This method has the advantage of ease of arithmetical calculation; it involves the handling of a minimum number of fractions, and requires *no* mixing of fractions of differing composition except as a result of irregularities in operation. 20

Results.—The work up to the present has been largely of a preliminary nature, but the features of design and operation have now been so far developed that additional radical changes are not to be anticipated. It seems desirable, therefore, to describe the method and apparatus at this time, as considerable time will be required to effect a large separation. The present preliminary separation, 0.01016 units of atomic weight on 22cc. (300g.) samples, was obtained in a few weeks of irregular operation with an incomplete set of units.²¹

Systematic Fractionation

A detailed study of systematic fractionation was found to be of prime importance in the design and operation of the apparatus. The most important results, given below, are applicable not only to the present

 20 These factors are enough to offset the slightly greater loss of diffusion value during collection, and the 17% greater capital stock required, as compared with the use of 30% fractions. The advantage of the use of 30% fractions in regard to amount of stock needed can be obtained only by constantly mixing fractions. The separation into 50% fractions involves a higher average flask-content, and so a somewhat higher efficiency, than the use of 30% fractions for operation at a fixed minimum volume of the residue.

²¹ The extreme samples consist of 22 cc. of material for which $\Delta M = +0.00504$ and 22 cc. for which it is -0.00512. The best result previously reported is that of Brönsted and Hevesy [Z. physik. Chem., 99, 189 (1921) and Phil. Mag., 43, 31 (1922)] who obtained 0.2 cc., $\Delta M = +0.0046$, and 0.3 cc., $\Delta M = -0.0052$. A far greater quantity has therefore been obtained in the present work although the quality of separation obtained in the two researches is about the same.

special method, but to all methods of the diffusion type (including evaporation).

Suppose a symmetrical fractionation procedure to be used for the division of an initially homogeneous sample into a set of fractions, all of size Q_0 , spaced at equal ΔM intervals on both sides of the initial composition (atomic weight) M_0 . The simplest procedure would consist of a series of individual or *unit* operations, in each of which a fraction of size $2Q_0$, and composition M, is divided into two fractions of size Q_0 and composition $M = EB \ln 2$. It can be shown by a study of the fractionation procedure, that when the first n-1 pairs of fractions have already been produced, a total of n^2 additional unit operations will be required to produce the n^{th} pair of fractions without permanently using up or increasing in size any of the previously produced fractions. The corresponding time expended in producing the n^{th} pair is evidently $t_n = n^2(Q_0/D)$, where D = dQ/dt, the rate of diffusion (or, in general, of production) of the light fraction.

Since
$$\Delta M = \pm nEB \ln 2$$
, (1)

$$t_n = (\Delta M)^2 Q_0 / DE^2 B^2 (\ln 2)^2,$$
 (2)

The time required to produce a pair of extreme fractions (or as can be shown, one of these) is thus proportional to the *square* of the difference between its composition and that of the original raw material, and *inversely* to the *squares* of the efficiency and of the separation coefficient. It can be shown that the same proportionalities hold for any type of fractionation procedure.

Since in the production of extreme fractions, intermediate fractions of sufficient size for efficient operation must be maintained (except as noted below) the time of production of any extreme fraction should be taken to include the total time of production of all intermediate fractions. Evidently,

$$t = t_1 + t_2 + \dots + t_n = (1^2 + 2^2 + 3^2 + \dots + n^2)(Q_0/D) = n(n+1)$$

$$(2n+1)(Q_0/6D)$$
(3)

This equation can be used to calculate the operating time required to obtain any given fraction of composition ΔM , if the corresponding value of n is calculated from Equation 1. The actual working time required will be about three times this. For n=1, t_n has the value n^3Q_0/D ; for n=5, 0.44 n^3Q_0/D ; for n=10, 0.38 n^3Q_0/D ; for $n=\infty$, $n^3Q_0/3D$. Approximately, then, t is proportional to n^3 , except for the smallest values of n. Then, approximately, from Equation 1 and the relation just deduced, t=K $(\Delta M)^3$ Q_0/DE^3B^3 (4).

Equation 4 contains a great deal of information. The other factors being constant, in each case, it shows (1) the rapidly increasing difficulty of increasing ΔM , even by systematic fractionation, which is the most rapid way of applying any method of the diffusion type; (2) the great

effect of the value of B (which depends on the element or compound used) on the possibility of obtaining a large separation ΔM in a moderate time; ²² (3) the importance of using a method and apparatus which can deal with small intermediate fractions (Q_0) , yet operate at high speed (D). ²³ Equation 4 also yields a criterion for the relative importance of speed, minimum operating volume (Q_0) and efficiency. Evidently for a given $\Delta M/B$, t will be a minimum if DE^3/Q_0 is a maximum. This criterion is of great value in both the design and the operation of any apparatus of the diffusion or of an analogous type. It was very useful in the development of the present apparatus.

The effect of the method of fractionation is not indicated by Equation 4, which was, in fact, developed above on the basis of a specific method consisting in a series of cuts of 2. It has already been stated, however, that, taking into account all practical factors, such a method of fractionation is probably more rapid than any other, and it is certain that no other fractionation procedure can have more than slight superiority. Equation 4 also does not take into account the possibility of using more than one type of apparatus in a single separation, that is, a rapid apparatus (one with large D) with large Q_0 in the earlier stages, and a slower, but also smaller, apparatus for the final stages. By such a method ΔM may be increased in a moderate time by a quite appreciable, although limited, amount with small quantities of material, the possible increase being proportional to B. In applying the criterion of the previous paragraph, the factors Q_0 , E and D must be considered in relation to the amount of time required for repairs and reconstruction and in emptying and refilling the apparatus, and in relation to losses by mixing unlike fractions, such as occur especially at refilling operations, in which complete removal of previous contents is impossible. It may be noted that the heavy fractions are here, and usually, somewhat easier to separate than are the light fractions, because of the more frequent emptying and refilling required by the latter,24 and for other reasons already noted. Although it is best to develop both fractions in equal amounts, either may be developed alone. In this case at least half the starting material must go into fractions which are left untouched after one or two operations.

Equation 2 or 4 may be made the basis of a criterion for the value of isotopic samples. The value of a fraction or set of fractions may perhaps best be considered as proportional to the time expended in producing it under standard, optimum, conditions of operation. On this basis, from Equation 2, the value of any individual fraction in a set of fractions may be defined as $V = (\Delta M)^2 Q$. V, thus defined, is an additive function.

²² Note that B varies with ΔM , causing a progressive decrease in the separation as it approaches completion. Also see Ref. 4.

²³ The tendency is, of course, for E and D to fall with Q_0 .

²⁴ This involves increased time and increased loss during mixing.

From a somewhat different point of view, which is particularly applicable to the *extreme* fractions, the value of an extreme fraction may be defined, ²⁵ on the basis of Equation 4, as $V' = (\Delta M)^3 Q$. Really, $V' = C \Sigma V$, the summation being taken over all fractions in a complete set up to and including the extreme fraction to which it is desired to assign a value, in the case of a symmetrical fractionation.

Results of the application of the first of the above definitions to a study of the loss of value by the collection of fractions of 30% or 50%, and by mixing separated fractions, have already been indicated. The loss of value when two samples of respective compositions $M + \Delta_1 M$, and $M + \Delta_2 M$, and quantities Q_1 and Q_2 , are mixed, is readily shown to be $-\Delta V = (\Delta_1 M - \Delta_2 M)^2 Q_1 Q_2 / (Q_2 + Q_2)$. This equation also holds for the gain of value when two separated fractions of different composition are produced from a single uniform sample.

In conclusion, the writer wishes to express his appreciation of the assistance of Mr. B. R. Mortimer in the operation of the apparatus, and of Mr. F. A. Jenkins in the purification of the mercury. The further operation and development of the apparatus will be in the hands of Mr. Mortimer and Professor W. D. Harkins.

Summary

- 1. An apparatus is described for the rapid partial separation of mercury into isotopes by a combined process of distillation and molecular diffusion, at low pressure, the latter process being the major factor in the separation. The diffusion membrane in each unit consists of a tube of filter paper 1 meter long, this material being selected primarily because of its thinness.
- 2. The operation of the apparatus is carried on as a systematic fractionation, in which 6 units are used independently. A set of connected units was considered, but rejected for several reasons.
- 3. Preliminary operation of the apparatus has given a separation of 0.102 units of atomic weight between extreme fractions of 22 cc. A separation of 0.3 units with 50 cc. fractions should be obtained in a year of steady work.
- 4. The method by which the new value 0.0063 for the separation coefficient of mercury was obtained is described in connection with the preliminary studies on the design of the apparatus.
- 5. Systematic fractionation requires the maintenance of a permanent stock of intermediate fractions, of some minimum size Q_0 , in order to extend the range of a separation. A thorough study of the course of systematic fractionation has yielded valuable results which are applicable to all methods of separation by diffusion or in an analogous manner.
- ²⁵ Aston ["Isotopes," Edward Arnold and Co., London, 1922, p. 139] has proposed the use of what is approximately $(\Delta M)Q$ as a measure of value; this has the disadvantage of not reflecting fully the difficulty of increasing ΔM .

The simple and symmetrical method of fractionation in which a cut of 2 is made in each individual operation is probably the most rapid for practical operation.

The time required for the production of any fraction, after the necessary preliminary or intermediate fractions have been produced, is given by the formula $t = C(\Delta M)^2 Q_0/DE^2B^2$, where E is the "efficiency," B the separation coefficient, D the rate of production of the light fraction, and C a constant. This serves to establish a criterion for the value (V) of any fraction, which may be defined as, $V = (\Delta M)^2 Q$. This criterion is applied to the calculation of loss of value by mixing, etc.

The time required for the production of any extreme fraction, taking into account the total time used in building up the intermediates, is given by $t = C'(\Delta M)^3 Q_0/DE^3 B^3$. Study of this equation shows the difficulty of obtaining large values of ΔM , especially if B is low. It also shows the relative importance of Q_0 , D and E, and this relation, somewhat modified by other practical considerations, was used in the design, and is also used in the operation, of the present apparatus. The optimum speed of operation is shown to be that for which $E^{3\cdot 5}D$ or E^4D is a maximum. The equation above can also be used as a basis for a criterion of value for extreme fractions, namely, $V' = (\Delta M)^3 Q$.

6. The approximate proportionality of the time required for a given separation to the *cube* of the degree of separation shows that while considerable separations can be effected by systematic fractionation, nothing approaching complete separation can be expected by methods of the diffusion type, unless in the most favorable cases and by factory-scale operation. It may be stated further that there seems to be little prospect that any other method or methods yet proposed will prove greatly superior to those of evaporation and molecular diffusion, although the centrifugal method may prove useful, especially for the elements of higher atomic weight.²⁶ For any particular element, the most favorable method depends greatly on the nature of the substance.

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²⁶ An ingenious method recently proposed by Hertz [Physik. Z., 23, 433 (1922)], while apparently very attractive in making possible an almost indefinitely large separation in one operation, can do so only at a rate of production that can be shown to decrease exponentially as the separation ΔM increases linearly. This, together with the relatively unfavorable ratio (Ref. 2, p. 1051) of the diffusion constants for gaseous, as compared with molecular diffusion, makes the apparent great superiority of the Hertz method extremely doubtful. The question reduces essentially to one of speed of production. The possibility of controlling the ΔM obtained in a single operation is however, certainly an advantage, as it gives a possibility of cutting down the volume of the intermediate fractions.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE SYNTHESIS OF AMMONIA FROM ITS ELEMENTS IN THE LOW-VOLTAGE ARC1

By H. H. STORCH AND A. R. OLSON Received March 16, 1923

Heidemann² reported the synthesis of ammonia from its elements as being initiated by electrons of a velocity corresponding to more than 2 volts, and less than the ionization potential of either gas. His papers contain little or no description of apparatus, and practically no data.

Subsequently Andersen³ studied the rate of reaction at various applied voltages. His plot of the change in pressure per unit of time against the accelerating voltage

led him to the conclusion that the reaction did not commence until the ionizing potential (about 17 volts) of nitrogen was reached. Andersen's curves were of a wave type, the maxima and minima rising with increasing voltage. The distance between adjacent maxima or minima was 4–7 volts. No explanation of the shape of these curves was given beyond the vague suggestion that this might be due to some auxiliary resonance phenomenon.

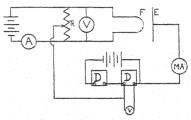


Fig. 1.—Electrical set-up

Andersen made no attempt to correct his voltages for the drop in potential along the tungsten filament used as a source of electrons. These drops were comparatively great, varying from 8 to 14 volts, and the corrections would, therefore, be of the order of magnitude of several volts.

In view of the unsatisfactory state of this problem, it seemed desirable to duplicate Andersen's apparatus, and attempt to find an explanation of the curves he obtained, using, however, much smaller potential drops across the cathode, and applying the accelerating potential at the center of the filament. The latter was done, as shown in Fig. 1, by applying the accelerating potential at the center of a resistance which was connected in parallel with the filament.

Experiments with an Apparatus Similar to that Employed by Andersen

The reaction chamber of the preliminary experiments was practically identical with that employed by Andersen.

It consisted of an 800cc. bulb into which were sealed 2 platinum plates to serve as anodes, and a tungsten filament acting as the source of electrons. Each anode was 1.5 sq. cm. in area, and the diameter and length of the filament were 0.050 and 2.5 cm., respectively. The filament was situated midway between the 2 platinum plates which were 1.5 cm. apart, thus making the distance between the cathode and anode 0.75 cm.

¹ This paper was constructed from a thesis presented by H. H. Storch to the Faculty of the Graduate School of the University of California in May, 1923, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Heidemann, Chem.-Ztg., 45, 1073 (1921); 46, 97 (1922).

³ Andersen, Z. Physik, 10, 54 (1922).

The total volume of the apparatus, including the McLeod gage and connections to the mercury vacuum pump, was approximately 1500 cc. A side tube containing 1 cc. of 98% sulfuric acid was attached to the bulb.

The electrical set-up is shown in Fig. 1. The voltmeters are designated by the letter V; A is an ammeter; MA a milliammeter; R is a 2000hm resistance; F represents the filament, and E the 2 anodes. The accelerating voltage was obtained from 4 sets of small lead storage cells, each set giving 50 volts, the 4 sets being connected in parallel. These batteries were short circuited through 2 dial resistance boxes (D, D), the sum of whose resistance was kept constant at 10,000 ohms. The accelerating voltage was controlled by connecting the tube electrodes to one of the dial resistance boxes, as a shunt circuit. The heating current for the filament was supplied by 2 sets of 5 Edison cells connected in parallel.

The hydrogen was obtained by the electrolysis of 10% potassium hydroxide solution, and was freed from oxygen by passage through a tube containing platinized asbestos. The nitrogen was prepared by removing the oxygen from air with alkaline pyrogallol. The gases were led into a mixing chamber and stored there over water. Before being admitted to the reaction chamber, the gas mixture was passed through a tube containing a glowing platinum wire, and through phosphorus pentoxide. The gas mixtures so prepared were found by analysis to contain only traces of oxygen, and no combustible gases other than hydrogen could be detected by the regular method of gas analysis.

The bulb was thoroughly "baked" and evacuated until the McLeod gage indicated a pressure of less than 10^{-4} mm. of mercury. The gas mixture (20% of hydrogen to 80% of nitrogen was used in this tube) was then admitted up to the desired pressure. Only one pressure was employed throughout, namely, about 0.17 mm. of mercury. The filament was kept at the temperature necessary to give a tube current (between E and F) of 0.6 milliampere at the particular voltage to be used in the determination. After having ascertained by pressure readings at 5-minute intervals that the pressure was not changing within the limits of the experimental error of reading the gage (which was $\pm 0\,0005\,\mathrm{mm}$. of mercury at 0.17 mm. total pressure), the accelerating voltage was turned on and the drop in pressure in 5 minutes was observed. The residual gas was then pumped out, and more of the original mixture admitted, the pressure being adjusted to within a few per cent. of that in the previous determination. The tube current was kept constant at 0.6 milliampere for all determinations.

Blank tests were, of course, made, using the separate gases at pressures corresponding to the partial pressures of the gases in the mixture. The changes in the pressure in the pure gases were found to be negligible, being only 1 to 3 times the error of reading the McLeod gage.

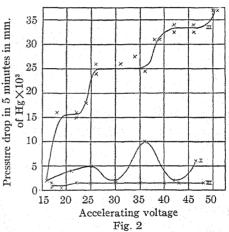
It was soon discovered that there are two phenomena which must be carefully considered in the interpretation of pressure drops in vacuum tubes containing a mixture of nitrogen and hydrogen, metallic electrodes and hot tungsten filaments. First, cold metals such as tungsten, copper, and especially nickel or platinum, will adsorb active hydrogen (produced by the hot tungsten wire) with great rapidity until the metal surfaces are in equilibrium with the partial pressure of active hydrogen present in the tube. Second, the efficiency of the absorption of ammonia by a sulfuric acid surface of small area is very low as compared with its absorption by the large surfaces of the glass walls of the vacuum tube, these surfaces being coated with an adsorbed film of sulfuric acid. Thus it was found that the sulfuric acid tube could be sealed off, and for a short

time the reaction rates observed were almost as great as with the sulfuric acid tube on.

It was further ascertained that wave curves of the type given by Andersen could be readily obtained when the glass surfaces were allowed to become saturated or nearly saturated with ammonia. This phenomenon will be referred to as the "fatigue" factor. For example, Curve I of Fig. 2 is of a wave type, and was obtained by measuring the change in pressure in 2 minutes at 17, 21, 25, 30, 36, 42 and 46 volts without evacuating the bulb after each determination. The observations were limited to 2 minutes and taken every 4 to 6 volts in order to avoid appreciable change in composition of the gas mixture. The drop in pressure for 5 minutes was calculated and plotted against the voltage.

When, however, the glass walls of the bulb were reheated, and the apparatus was thoroughly evacuated after each rate determination, the data

indicated, as shown in Curve II of Fig. 2, that the rates were approximately constant for given voltage intervals, and that abrupt increases occurred at specific voltages. Hence, the explanation of the wave type of curve obtained by Andersen is obviously that the fatigue factor distorted what would otherwise have been a "step-like" curve. In the type of apparatus employed by Andersen the fatigue factor was found to be too rapid in its action to admit of any accurate determina-



tion of the voltage intervals corresponding to the sudden increases in reaction rate. Thus the individual points of Curve II were not accurately reproducible and, as will be shown later, the fatigue effect blurred out most of the breaks that exist in the region between 20 and 50 volts. Although a smooth curve approximately quadratic would fit the observations represented in Curve II, the results of later work made it seem more reasonable to draw the curve as shown. Curve III of Fig. 2 shows the pressure changes in the separate gases at various voltages.

The following facts were also established in the preliminary experiments. Positive tests for ammonia with Nessler's reagent were obtained at as low a voltage as was necessary to start an arc in the tube. With the distance between the filament and the platinum anodes at 0.75 mm., this voltage was usually 18 volts, but it was occasionally possible, by jarring the tube slightly, to start an arc at 16 volts, and obtain a satisfactory positive test

for ammonia at this voltage. At voltages lower than 16–18 volts the pressure drops taken over periods of 2 minutes were found to be of the order of magnitude of those observed in the separate gases, and the tests for ammonia with Nessler's reagent were negative.

At the beginning of the preliminary experiments the tungsten filament was 0.050 cm. in diameter, but it gradually became thinner due to the spluttering and evaporation of tungsten. At the same time it was noted that the rate of the reaction at a given voltage increased slowly with the time. The possibility of a direct connection between these two observations led to an investigation of the effect of the diameter of the filament on the reaction rate. The results obtained are summarized in Table I. The 5 experiments were made with the same apparatus (similar to that used by Andersen, and as described above), but a different filament was employed for each experiment.

Table I

Variation of Rate of Reaction with the Diameter and Temperature of the Filament at Constant Pressure

Pressure, 0.17 mm. of Hg; tube current, 0.6 milliampere; voltage, 18 volts.

E	xpt.	Diam. of filament Cm.	Length of filament Cm.	Potential drop across filament Volts	Current through filament Amperes	Pressure drop in 5 minutes Mm. of Hg
	1	0.050	5.0	3.50	13.0	0.005
	2.	.030	6.25	3.95	4.9	.008
	3	.030	3.13	2.45	6.5	.008
	4	.0125	3.13	4.00	1.0	.010
	5	.005	2.5	5.32	0.55	.013

It will be observed that the thinner filaments gave the higher rates of reaction. That this was not due to the higher temperature of the thinner wires is proved by comparing Expts. 2 and 3. In No. 3 the filament was hotter than in No. 2, but of the same diameter, and the reaction rates are identical. The explanation of these observations is probably that the potential gradient in the arc is very steep near the cathode, and hence the electrons acquire most of their energy at a very short distance from the filament, thus causing most of the ammonia to be formed in this region. The diameter of the wire, therefore, would largely determine the chance which an ammonia molecule has to escape decomposition by the hot filament, and in this way control the rate of the reaction.

In these experiments with excess of nitrogen (4 to 1) the total drop in pressure at any given voltage (above that necessary to start the arc) was much greater than could be accounted for by the complete removal of the hydrogen introduced for the experiment. This was due to the fact that the platinum anodes provided an additional supply of hydrogen by giving up their adsorbed hydrogen during the course of the reaction. Thus it was found that when a tube was used in which a mercury surface

was the anode (see below), the total pressure drop was identical with that calculated from the composition of the gas mixture.

Experiments with a Mercury Anode and a Glass Wool Surface

The chief difficulties encountered in the type of apparatus similar to that used by Andersen were: (1) the fatigue of the absorption mechanism was rapid; (2) the quantities of hydrogen absorbed by the platinum anodes were relatively large, and hence the equilibration of the anodes before each determination was a very necessary and tedious procedure.

The apparatus shown in Fig. 3 was designed to eliminate both of these objections.

As indicated in the diagram, the mercury level (F) which served as the anode could be raised or lowered at will, thus making it possible to vary the distance between the electrodes without reconstructing the apparatus. The U-shaped filament is drawn in perspective to indicate its shape; the plane determined by the sides of the U was parallel to the mercury surface. The space A was filled with glass wool, in order to increase the adsorption surface and thus reduce the fatigue effect. The side tube E contained 1 to 2 cc. of 98% sulfuric acid. A condenser was attached below the reaction chamber in order to keep the temperature of the mercury constant. A 500cc. bulb was sealed into the line, in order to bring the total volume of the apparatus up to 1500 cc.

The clean-up of nitrogen during a 5- or 10-minute interval was found to be very small compared with the pressure drops in the gas mixture. (See similar data in Table V for a later apparatus.) The adsorption of hydrogen by the metal parts in this tube was very low, being practically within the experimental error of reading the gage. The other difficulty, namely, the fatigue effect, was, however, not entirely eliminated.

Before beginning the rate determinations the tube was thoroughly baked and evacuated as before, but it was found impossible to remove the adsorbed gas completely from the glass wool. However, after a few hours'

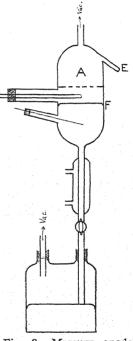


Fig. 3.—Mercury anode apparatus

baking and pumping it was found that the glass wool no longer gave off any measurable quantity of gas during the course of several hours with 0.17 mm. of mercury pressure of the gaseous mixture in the tube.

The procedure used in making the rate determinations was the same as that outlined above for the first apparatus, except that a greater tube current, namely 1 milliampere, was used. In this latter apparatus the filament was 0.0125 cm. in diameter, and 1.25 cm. long.

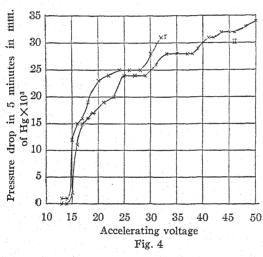
As shown in Table II, the rate of reaction at 18 volts, with the electrodes 4 mm. apart, and with no sulfuric acid present, was found to be only 1/3 as great as the rate with the sulfuric acid present. The glass wool was not in contact with the liquid sulfuric acid.

Table II Adsorption of Ammonia by the Glass Wool Surface

Electrodes 4 mm. apart. Composition of gas: H₂, 32%; N₂, 68%. Initial pressure, 0.170 mm. of Hg; 18 volts accelerating voltage; tube current, 1.0 milliampere.

	Pressure drop	Filament			
	in 5 minutes Mm. of Hg.	Voltage Volts	Current Amperes		
No H ₂ SO ₄	0.008	1.50	2.70		
With H2SO4	.024	1.47	2.65		

Since in this tube the clean-up of the separate gases was found to be negligible during a 5-minute interval, it follows from the data of Table II and the observations made with the first apparatus that the mechanism of the absorption of ammonia is 3-fold, namely, (1) adsorption by the glass surfaces; (2) reaction with the sulfuric acid adsorbed on the glass surfaces; (3) reaction with the sulfuric acid surface itself.



The results obtained with this tube are sketched in Fig. 4. Curve I represents the data obtained with a 14.3-85.7% mixture of hvdrogen and nitrogen and Curve II those with a 32-68% mixture. With the electrodes 3 mm. apart it was possible to start the arc at 15 volts, and a satisfactory positive test for ammonia was obtained at this 50 voltage. With the electrodes 7 mm. apart the arc could not be started below

18 volts, and a negative test for ammonia was obtained below 18 volts. Hence, it seems that the formation of ammonia does not occur to any appreciable extent unless an arc is present.

A comparison of Curves I and II of Fig. 4 shows that the rate of the reaction is greater for a lower hydrogen content, which is in accord with the results obtained by Andersen. Curve II clearly indicates that the rate of ammonia formation remains approximately constant for definite voltage intervals, and increases abruptly at certain voltages. The individual points of this curve were not reproducible, but the general shape of the curve could be fairly well duplicated.

The individual points of the curves in Fig. 4 were not reproducible largely because of the fatigue effect. Reheating the glass wool after each determination caused erratic results because the glass surfaces could never be freed entirely of their adsorbed gases. Hence the curves of Fig. 4

were obtained by allowing the glass wool to become fatigued, that is, by not reheating after each determination. The fatigue factor was, however, slow enough in its action to prevent distortion into the wave type of curve.

Experiments with a Copper Gauze Anode, Using a Liquid-air Bath to Remove the Ammonia Gas

To avoid the fatigue factor it was decided to construct a discharge tube that could be entirely immersed in a liquid-air bath, so as to freeze the ammonia as fast as it was formed, thus making it possible to abandon the use of glass surfaces and sulfuric acid as the absorption device.

The apparatus consisted of a small tube containing a copper gauze anode and the tungsten filament. The tube was 2.5 cm. in diameter and 10 cm. long. The anode was made of 1 mm. mesh copper gauze, was cylindrical in shape, and was 8 cm. long. The tungsten filament was 0.0125 cm. in diameter and 1.25 cm. long. The distance from the center of the filament to the anode was approximately 10 mm. The total volume of the apparatus, including the McLeod gage, and a 750cc. bulb, was approximately 1500 cc. The tube containing the electrodes was completely immersed in liquid air during the rate determinations.

The copper anode was found to adsorb comparatively little hydrogen, but it was noted that the amount taken up was considerably greater than in the previous tube containing a mercury anode. As in the case of the first tube containing platinum anodes, the total pressure drop in this last tube was considerably greater than that calculated from the composition of the gas mixture, thus confirming the explanation of this phenomenon, given in a previous paragraph.

The pressure drops observed in the separate gases are given in Table III. It will be observed that the drops at the various voltages up to 50 volts are practically identical. This proves that the increases in rate observed with the mixture of the 2 gases were not due to abrupt increases in the adsorption of hydrogen by the metal and glass surfaces of the discharge tube, nor in the clean-up of nitrogen by the hot tungsten filament.

TABLE III

BLANK TESTS WITH THE SEPARATE GASES AT VARIOUS VOLTAGES, AT CONSTANT TUBE
CURRENT

Current, 1 milliampere; distance between electrodes, 10 mm.; diameter and length of filament, 0.0125 cm. and 1.25 cm., respectively.

	1	VITROGEN		
Initial pressure Mm. of Hg	Pressure drop in 5 minutes Mm. of Hg	Accelerating voltage Volts	Volts Filan	ment——— Amperes
0.104	0.001	20	1.7	1.90
.117	1	30	1.3	1.65
.117	2	41	1.23	1.60
.115	2	52	1.10	1.57
	Ī	Hydrogen		
.065	.002	20	1.23	1.70
.062	2	30	1.15	1.65
.062	2	40	1.10	1.60
.059	2	50	1.08	1.60

It was found necessary to bombard the copper gauze anode for about an hour with a heavy electron current (1 to 3 milliamperes) in a high vacuum before starting the rate determinations. If this precaution was not observed, the apparent rates of reaction were low, and not reproducible. This bombardment should be conducted at room temperature, or preferably at $300-400^{\circ}$, for at the temperature of liquid air the time necessary for the complete removal of all foreign gases from the anode was extraordinarily long.

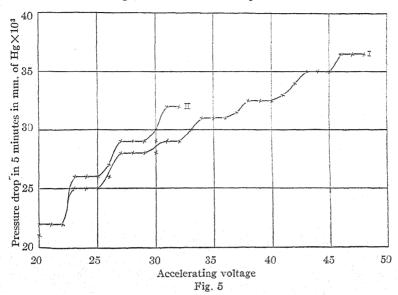
Table IV

Rates of Reaction at Various Voltages at Constant Tube Current
Current, 1 milliampere; distance between electrodes, 10 mm.; diameter and length
of filament, 0.0125 cm. and 1.25 cm., respectively; filament current and voltage drop,
1.10-1.24 ampere, 1.03-1.30 volt. Composition of gas: H₂, 32%; N₂, 68%.

Initial pressure Mm. of Hg	Pressure drop in 5 min. Mm. of Hg	Accelerating voltage Volts	Initial pressure Mm. of Hg	Pressure drop in 5 min. Mm. of Hg	Accelerating voltage Volts
0.166	0.022	20	0.169	0.029	30
. 167	.022	20	.167	.029	31
165	.022	21	.167	.029	31
. 169	.022	21	.168	.029	32
169	.022	22	.168	.029	32
.169	.022	22	.169	.030	33
.162	.025	23	.168	.031	34
.167	.025	23	.168	.031	35
.169	.025	24	.168	.031	36
.167	.025	24	. 167	.0315	37
.166	.025	25	.166	.0325	38
166	.025	25	.168	.0325	39
.167	.027	26	.169	,0325	40
.170	.026	26	.167	.033	41
.162	.028	27	. 169	.034	42
.166	.028	27	.168	.035	43
.165	.028	28	.170	.035	44
. 166	.028	28	. 169	.035	45
. 169	.028	29	.168	.0365	46
.167	.028	29	.168	.0365	47
. 166	.028	30	.168	.0365	48

Table IV gives the results of two series of determinations made with the same filament. The first series shows the rates taken at 1 volt intervals from 20 volts (the arc could not be started below 19 volts in this tube) up to 32 volts, and the second series up to 48 volts. The data were found to be reproducible within the experimental error of reading the pressure gage. These results are graphed in Curve I of Fig. 5. Table V gives a third series of measurements (plotted in Curve II of Fig. 5) up to 32 volts, using a different filament. The results, except for the 20–22 volt points, run uniformly higher than those of Table IV. This is probably to be explained by the variation in the diameters of the filaments, for the filament used in obtaining the data of Table V burned out shortly after the 32-volt determination was made, and hence it was probably thinner

than the filament of Table IV. A comparison of the 2 curves of Fig. 5 shows that the voltages at which the abrupt increases in the rate of the



reaction occur, are accurately reproducible, even when different filaments are employed.

Table V
Rates of Reaction at Various Voltages at Constant Tube Current
Current, 1 milliampere; distance between electrodes, 10 mm.; diameter and length
of filament, 0.0125 cm. and 1.25 cm., respectively; filament current and voltage drop,
1.48–1.51 ampere, and 1.05–1.22 volt. Composition of gas: H₂, 32%, N₂, 68%.

Initial pressure Mm. of Hg	Pressure drop in 5 min. Mm. of Hg	Accelerating voltage Volts	Initial pressure Mm. of Hg	Pressure drop in 5 min. Mm. of Hg	Accelerating voltage Volts	
0.167	0.021	20	0.163	0.027	26	
.174	.022	21	.172	.029	27	
.173	.022	22	.166	.029	28	
.173	.026	23	.169	.029	29	
.170	.026	24	.169	.030	30	
.170	.026	25	.173	.032	31	
			.171	.032	32	

Discussion

The data given in the last two tables indicate that the rate of the reaction, after the arc is once formed, increases abruptly at the following voltages: 23, 26–27, 30–31, 33–34, 37–38, 41–42 and 46. The intervals between these voltages are about 4 volts each. This phenomenon may be characteristic of the reaction, or it may be dependent upon the particular type of apparatus employed. The latter explanation seems improbable because

the data obtained with the mercury anode apparatus also gave a "step-like" curve whose shape was reproducible. Moreover, the work on ionizing and resonance potentials shows that the voltage at which abrupt changes in the slope of current-voltage curves occur are characteristic of the gas employed.

The fact that an arc is essential for an appreciable formation of ammonia to occur makes it probable that ionized hydrogen or nitrogen, or both, are necessary before the reaction will proceed. Indeed, it is possible by various combinations of the critical potentials, observed in ionization tubes, for nitrogen and hydrogen, to account for the abrupt increases in the rates of reaction. Thus the 23-volt point may be due to increased ionization of nitrogen by electrons which have first produced resonance in nitrogen, and then gained sufficient energy to ionize nitrogen. However, these 4-volt points may be due to a critical point which is not directly observed in ionization tubes, such as the dissociation of molecular hydrogen or nitrogen.

In conclusion, therefore, we may state that the explanation of the phenomena presented in this paper must await such further research as a detailed study of the spectrum of the arc in a mixture of nitrogen and hydrogen, and the study of other reactions involving nitrogen or hydrogen.

This work was begun while one of the authors (A. R. O.) was a National Research Fellow in chemistry. We take this opportunity to express our appreciation to the National Research Council.

Summary

A study of the factors which control the rate of formation of ammonia from nitrogen and hydrogen in the low-voltage are yielded the following results.

- 1. The results of the earlier work by Andersen in which a wave type of curve was obtained for the rate of reaction as a function of the accelerating voltage are explained by the preliminary experiments described in this paper. The curve obtained by Andersen was found to be due to a superposition of the curve described in 2 (below), and a "fatigue" factor in the mechanism used for absorbing the ammonia gas.
- 2. The variation of the rate of the reaction, at constant tube current with the accelerating voltage, is such as to give abrupt increases in the rate of the reaction at specific voltages which are about 4 volts apart.
- 3. The formation of ammonia in sufficient quantity to be detected by Nessler's reagent does not occur unless an arc is present.
- 4. The magnitude of the rate at any given voltage, and at constant tube current, depends primarily on the diameter of the hot filament used as the source of electrons.
 - 5. An increased nitrogen content favors a higher rate of reaction.

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THE TITRATION OF SOLUTIONS OF PERMANGANATE AND SODIUM ARSENITE

By WILLIAM T. HALL AND CARL E. CARLSON

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The manganese content of iron, steel and other alloys is frequently determined by oxidation to permanganate followed by titration with sodium arsenite solution. It has often been assumed that the titration reaction may be expressed as follows: $2\text{MnO}_4^- + 5\text{HAsO}_3^{--} + 6\text{H}^+ \rightarrow 2\text{Mn}^{++} + 5\text{HAsO}_4^{--} + 3\text{H}_2\text{O}$. This equation assumes oxidation of the tervalent arsenic to the quinquivalent condition and reduction of the permanganate to manganous salt; each atom of maganese furnishes 5 oxidation equivalents and each atom of arsenic requires 2.

In fact, Bussy³ and Moser and Perjatel⁴ have titrated arsenite with permanganate in hydrochloric acid solution and found the above reaction correct. Vanino,⁵ Kuhling,⁶ and Klemenc⁷ have pointed out, however, that the oxidation of the arsenite toward the end of the titration is very slow. The first two have established the fact that the rate of reaction is accelerated by heating the solution nearly to boiling. Lang⁸ has recommended the addition of a little chloride or bromide to hasten the reaction.

Pean de St. Gilles⁹ carrying out the same titration under different conditions obtained a brown precipitate containing manganese probably in the quadrivalent state. Lenssen, ¹⁰ Kessler, ¹¹ and Brauner¹² titrated an arsenite solution with permanganate and found the oxidation of the arsenite complete but the permanganate only reduced to the tervalent manganic condition. This corresponds to a loss by each atom of manganese of 4 oxidation equivalents. On the other hand, Waitz¹³ found that in a sulfuric acid solution the permanganate appeared to lose 4.5 oxidation equivalents.

In the reverse titration of permanganate with arsenite solution Kessler obtained an olive-green solution and each molecule of permanganate appeared to lose 3.5 oxidation equivalents. In the analysis of steel by the Volhard method Deiss¹⁴ found permanganate is reduced to a state intermediate between $\rm Mn_2O_3$ and $\rm MnO_2$. Recently Bose¹⁵ in his

¹ Compare Proc. Am. Soc. Test. Materials, 1915, 210.

² Hall and Williams, "The Examination of Iron, Steel and Brass," McGraw-Hill Book Co., 1921.

³ Bussy, Compt. rend., 24, 774 (1847).

⁴ Moser and Perjatel, Monatsh., 33, 751 (1912).

⁵ Vanino, Z. anal. Chem., 34, 426 (1895).

⁶ Kuhling, Ber., 34, 404 (1901).

⁷ Klemenc, Z. anal. Chem., 61, 448 (1922).

⁸ Lang, Chem.-Ztg. Rep., 48 (1905).

⁹ de St. Gilles, Ann. chim. phys., 55, 385 (1859).

¹⁰ Lenssen, J. prakt. Chem., 78, 197 (1859).

¹¹ Kessler, Pogg. Ann., 118, 17 (1863).

¹² Brauner, Z. anal. Chem., 55, 242 (1916).

¹³ Waitz, ibid., 10, 174 (1871).

¹⁴ Deiss, Chem.-Ztg., 34, 237 (1910).

¹⁵ Bose, Chem. News, 117, 379 (1918).

study of the reaction found the manganese reduced only to an average valence of 3.3, and Geloso¹⁶ titrated permanganate in a sulfuric acid solution with arsenite and obtained the same result. He also worked to an emerald-green end-point and determined the acidity limits within which this end-point could be obtained. He found that sulfates of zinc, nickel, aluminum, magnesium and potassium had no effect upon this end-point, but those of manganese and silver did.

In order to overcome the slow rate of reaction between permanganate and arsenite, to eliminate a colored precipitate or solution which obscures the end-point and to complete the reduction of the manganese to the manganous state, several indirect titrations have been proposed. These depend on adding an excess of permanganate and titrating the excess with some reducing agent. For a reducing agent Pean de St. Gilles used a ferrous salt, Vanino and Kano¹⁷ hydrogen peroxide, and Brauner and Klemenc oxalic acid.

This review of the literature on the titration of sodium arsenite and permanganate solutions shows that it is possible under certain conditions to make the reaction take place according to the above equation, but the conditions are certainly different from those that prevail in an ordinary steel analysis. The accelerating effect of an excess of acid might be predicted from the above equation on the basis of the mass-action principle. On the other hand, experience with the iodimetric titration of arsenic indicates that in neutral or alkaline solutions the arsenate anion is more stable than the arsenite anion, but in strongly acid solutions the tervalent arsenic cation appears to be formed easily by reduction of the arsenate anion. Apparently an excess of acid favors the reduction of the manganese to the manganous condition more than it hampers the oxidation of the arsenic, and hydrochloric acid favors the reduction of tervalent and quadrivalent manganese more than sulfuric acid does. The retardation of the reaction in the presence of considerable acid must be due to the difficulty of oxidizing the arsenite in the presence of much acid.

Experimental Part

Inasmuch as most of the previous work has been with solutions containing sulfuric or hydrochloric acid and since in steel analysis nitric acid is most commonly used, it was of interest to study the reaction under conditions more nearly approximating those of procedures in which the sodium arsenite titration has been recommended for titrating the permanganate formed from the manganese in a sample of steel. The problem was first attacked by two students in quantitative analysis who had not had previous experience with the titration and who had practically no knowledge of the literature on this titration.

Mr. A. Cohen prepared a $0.0222\,N$ solution of sodium arsenite. Several portions of this solution were titrated under conditions similar to those obtained in the analysis of steel by the bismuthate method except that all the titrations were made in the permanganate. Upon the addition of

¹⁶ Geloso, Compt. rend., 171, 1145 (1920).

¹⁷ Kano, J. Chem. Soc. Japan, 42, 699 (1921).

permanganate the colorless solutions became vellowish-green, turning to a clear green just before a distinct pink color was obtained by an excess of permanganate. After standing for an hour or more the titrated solutions became a muddy brown and some manganese dioxide was precipitated. The analyses indicated a reduction corresponding to the formation of the compound Mn₂O₃.2MnO, thus agreeing with the work of Waitz. The results varied within about 3% of the total volume of permanganate used and were not sufficiently close to justify the adoption of this titration as a standard method of procedure. Attempts to carry out the titration under the conditions which prevail in the persulfate method for determining manganese, namely, in a solution containing 1.5 N sulfuric acid and 0.03 N nitric acid, resulted in a reduction of permanganate to approximately the dioxide. Experiments were also tried to determine the effect of adding manganous sulfate solution used in the Zimmermann-Reinhardt method for titrating iron. The results were very erratic although in one case a normal reduction of the permanganate was obtained.

Mr. C. F. Schell carried out a series of experiments which are summarized in Table I. No attempt was made to duplicate the conditions prevailing

	Soln. co	ntoined			
	100 cc. of			alence of	
	Coned. H ₂ SO ₄ Ce.	KMnO ₄ Cc. 1	Mn emperature	in reduced state	Remarks
			•		
1	5	20	cold	3.35	A clear green obtained with 24
					cc. of Na ₂ HAsO ₃ and no fur-
					ther change on adding 50 cc.
2	5	20	hot	4.02	KMnO ₄ reduced to MnO ₂
3	10	20	hot	3.6	Acid served to retard the oxida-
			*		tion of the arsenic
4	7	20	hot	3.8	
5	25	. 20	cold		No reduction
	Coned.	HC1			
6	5	20	hot		Decomposed before adding any
					arsenite
7	5	20	cold	2.94	Upon adding an excess of ar-
					senite the green color dis-
					appeared
8	5	20	cold	3.15	
	6 N ace		cora	0.10	
		LIC .	-13		Soln, turned brown with 7 cc. of
9	10		cold		
					arsenite; no further change with 50 cc. Soln. too faintly
					acid
	Concd.	H-SO.			나라 집에 얼룩하다 하는 아니다. 이번 하루
- 10			13	9.7	Excess of arsenite titrated with
10	5	24.62	cold	3.7	지수는 사람들은 사람들은 내가 되는 사람들은 사람들이 가는 그를 가는 것이 되었다. 그렇게 되었다.
					KMnO ₄

in steel analysis but the results show the need for carefully specifying the conditions of titration if the sodium arsenite reaction is to continue in favor as a means of determining the amount of permanganate in solution.

Electrometric Titrations

After these preliminary experiments by Cohen and Schell the titration was studied electrometrically. Kelley and his co-workers 18 found that permanganate formed in the analysis of steel can be titrated electrometrically with mercurous nitrate solution and the reduction corresponds to the formation of Mn_4O_7 ($Mn_2O_3.2MnO_2$) in which the average valence of the reduced manganese is 3.5.

An arsenite solution was prepared of the concentration recommended by the American Society of Testing Materials for the routine analysis of steel. It was titrated against an iodine solution which had been standardized against potassium bromate. A permanganate solution was prepared in the usual way and standardized against sodium oxalate. The ratio between the permanganate and the arsenite solution was also checked by indirect titration with hydrogen peroxide. Table II shows the results obtained in the electrometric titration when a solution of 25 cc. of permanganate and 100 cc. of nitric acid, d. 1.13, was titrated with arsenite. A tungsten electrode was substituted for the calomel, after the first few determinations, in order to eliminate any effect on the end-point due to the presence of potassium chloride.

Table II

	ELECTROM	ETRIC TITRATION	IN NITRIC AC	ID SOLUTION	1	
KMnO4,	0.1133 N A	rsenite, 0.09641 I	V KMnO ₄ , 0.1	133 N Ars	enite, 0.0964	1 N
KMnO ₄ Ce.		Valence of Mn in the reduced state	KMnO ₄ Cc.		alence of Mn he reduced stat	
	Calomel elec	trode	Tun	gsten electro	de	
24.92	22.29	3.197	24.92	21.80	3.278	
24.92	22.18	3.216	24.92	21.79	3.280	
24.92	22.11	3.223	24.95	21.87	3.270	
24.92	22.11	3.223	24.94	21.76	3.287	
24.92	22.22	3.204	24.95	21.75	3.290	
		Acceptance of the Control of the Con			***************************************	
		Av. 3.213		A	v. 3.281	

The next set of determinations was made with 100 cc. of sulfuric acid of various concentrations, substituted for the nitric acid.

To determine whether potassium chloride had any marked effect on the end-point a series of determinations was made by adding various amounts of potassium chloride to $100~\rm cc.$ of 2.5~N sulfuric acid and $25~\rm cc.$ of 0.1133~N permanganate solution and titrating with 0.09641~N arsenite solution. The theoretical volume of arsenite required was calculated

¹⁸ Kelley, J. Ind. Eng. Chem., 10, 19 (1918).

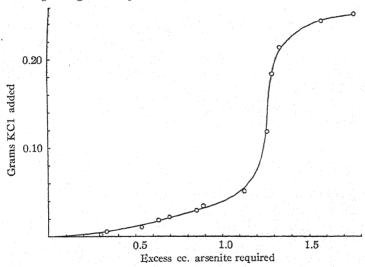
¹⁹ A Wendt titration apparatus was used for these titrations.

TABLE III

	Ele	CTROMET	RIC TITRATION	IN SULFUR	ic Acid S	COLUTION	
KMnO4,	$0.1133\ N$	Arsenite	e, 0.09641 N	KMnO4,	0.1133~N	Arsenit	e, 0.09641 N
Conc. of H ₂ SO ₄ N	KMnO ₄ Ce.		Valence of Mn in the reduced state	Conen. of H_2SO_4 N	KMnO ₄ Cc.	Arsenite Cc.	Valence of Mn in the reduced state
1	24.98	21.56	3.326	3	25.03	21.59	3.330
1	24.93	21.46	3.337	4	24.96	21.59	3.320
3	24.95	21.63	3.311	2.5	24.96	21.55	3.327
6	24.99	21.74	3.299	2.5	24.92	21.37	3.349
3	25.10	21.67	3.326	3	24.96	21.43	3.347
3	24.92	21.41	3.344	2.5	24.98	21.42	3.351

Av. 3.331

from the volume of permanganate, assuming a reduction to 3.333 as established in the above series of determinations. In the accompanying plot, the excess of arsenite in cubic centimeters is shown plotted against the weight in grams of potassium chloride added.



Finally a few titrations were made with the arsenite in 100 cc. of 2.5~N sulfuric acid and the permanganate as the titrating solution.

TABLE IV

		TUDH	3 1 4		
	REVERSE '	TITRATION IN S	ULFURIC ACID	SOLUTION	
KMnO ₄ , 0.113	3 N Arseni	te, 0.09641 N I	KMnO ₄ , 0.1133	N Arser	nite, 0.09641 N
KMnO ₄ Cc.	Arsenite Cc.	Valence of Mn in the reduced state	KMnO ₄ Cc.	Arsenite Cc.	Valence Mn in the reduced state
23.63	24.90	2.517	23.55	24.90	2.501
23.55	24.90	2.501	23.60	24.90	2.511
					5

Av. 2.507

All of these electrometric titrations were made at room temperature.

Summary

Under the conditions that usually prevail in the analysis of steel, the electrometric titration of permanganate with sodium arsenite solution causes the manganese to be reduced from a valence of 7 to an average valence of 3.3 when the bismuthate method is used. This agrees with the results obtained by Bose and by Geloso. The reaction between the permanganate may be expressed as follows: 6 MnO₄⁻ + 11 H₂AsO₃⁻ + $15 \text{ H}^+ \longrightarrow 2 \text{ Mn}^{+++} + 4 \text{ Mn}^{+++} + 11 \text{ HAsO}_4^{--} + 13 \text{ H}_2\text{O}$. The reduced condition corresponds to the oxide Mn₃O₅ but it is improbable that such an oxide actually exists. The color of the solution indicates the presence of tervalent manganese and the fact that manganese dioxide often separates on standing shows that the quadrivalent manganese readily assumes the condition of colloidal dioxide and finally forms the gel. Probably this reaction takes place: 2 Mn++++ + 4 $Mn^{+++} + 8 H_2O \longrightarrow 2 Mn^{++} + 4 MnO_2 + 16 H^+$. The fact that halide causes a more complete reduction of the manganese is in accord with the usual behavior of halogen hydride in permanganate titrations. It prevents the formation of colloidal dioxide and keeps the manganese in a more reactive condition.

The electrometric titrations show that when arsenite is titrated with permanganate in 2.5 N sulfuric acid solution the manganese is reduced to an average valence of 2.5 just as Waitz found more than 50 years ago. $4 \, \mathrm{MnO_4^-} + 9 \, \mathrm{HAsO_3^-} + 14 \, \mathrm{H^+} \longrightarrow 2 \, \mathrm{Mn^{++}} + 2 \, \mathrm{Mn^{++}} + 9 \, \mathrm{HAsO_4^-} + 7 \, \mathrm{H_2O}$. Whenever the reaction between permanganate and arsenite is used in practice to determine either manganese or arsenic it is important to pay attention to such details as temperature, acid concentration and presence of halide or manganous salt and to standardize the solutions under exactly the same conditions that prevail in the analysis.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 25]

THE CRYSTAL STRUCTURES OF THE CUBIC FORMS OF ARSENIOUS AND ANTIMONOUS OXIDES

By RICHARD M. BOZORTH Received March 26, 1923

Introduction

Octahedral crystals of arsenious oxide were prepared by slowly cooling a solution of the substance in hydrochloric acid with the addition of a small amount of sodium chloride. A crystal of the cubic form of antimonous oxide, senarmontite, from Mt. Hamimat, Algeria, was kindly supplied by Dr. G. P. Merrill of the National Museum. A careful qualitative examination of a part of this crystal carried out in accordance with the scheme of A. A. Noyes¹ showed about 3% of arsenic, about 10% of alkaline earths and a trace of bismuth.

The Spectral Photographs of Arsenious Oxide

Photographs were taken of line spectra reflected from (100), (110) and (111) faces. The results are given in Table I. Measurements are for the rhodium $\kappa \alpha_1$ line whose wave length was found by Duane? to be 0.6121 Å.

TABLE I
REFLECTION DATA FOR ARSENIOUS OXIDE

Reflecting	Angle of	Estimated	Order of	Length of		ed structu = 0.895, v	re factors for = 0.21	or
plane	reflection	intensity	reflection	unit cube	S_{As}	S_{0x}	S	
(100)	6°21′	strong	4	11.07	-112	40	-72	
	12° 49′	medium	8	11.04	69	25	94	
(110)	4° 29′	very weak	2	11.07	8	33	41	
	9° 0′	medium	4	11.07	98	2	100	
	13° 36′	weak	6	11.04	60	0	60	
(111)	2°46′	weak	1	11.0	24	8	32	
	5°30′	very strong	2	11.06	116	0	116	1
	8° 17′	medium weak	3	11.04	64	-23	41	
	11° 2′	medium stron	g 4	11.08	- 86	19	- 67	
	13°51′	medium weak	5	11.07	- 87	32	- 55	
		absent	6		- 50	0	- 50	
	19° 35′	very weak	7	11.07	- 89	-33	-122	

A consideration of these data shows that the smallest possible unit cube is 11.06 Å. on an edge. The orders of reflection given in Table I are on this basis. Combining these measurements with the density, which was found by Baxter and Hawkins³ to be 3.865, we find that this unit

¹ Noyes, "Qualitative Chemical Analysis," 8th ed., The Macmillan Co., New York, 1920.

² Duane, Nat. Research Council Bull., 1, No. 6 (1920).

³ Baxter and Hawkins, This Journal, 38, 269 (1916).

must contain 32 arsenic atoms and 48 oxygen atoms. A larger unit would contain 256 arsenic atoms and 384 oxygen atoms, and in this case neither the arsenic atoms nor the oxygen atoms could all be equivalent. Since no X-ray reflections were found which necessitated this larger unit, the smaller one was considered the true one.

The density calculated from the spectral measurements is 3.861, in good agreement with the observed value.

The Spectral Photographs of Antimonous Oxide

The results of the reflections of the molybdenum $\kappa \alpha_1$ line, of wave length² 0.7078 Å., from a (111) face of the crystal, are given in Table II.

	Table II	
REFLECTION	Data for Antimonous Oxide	

Angle of	Estimated	Calculated structure factors for $u = 0.885, v = 0.23$				
reflection	intensity	reflection	unit-cube	$S_{\mathbf{Sb}}$	S_{Ox}	S
3° 9'	very weak	1	11.15	22	4	26
6° 19′	strong	2	11.14	203	0	203
9° 29′	very weak	3	11.15	57	-12	45
12° 43′	medium	4	11.14	-189	42	-147
15° 59′	weak	5	11.13	- 90	20	- 70
19° 17′	medium weak	6	11.14	-167	0	-167

The unit cube of antimonous oxide is thus found to be 11.14 Å. on an edge. With 32 antimony atoms and 48 oxygen atoms in the unit, the density calculated from these measurements is 5.11. Direct determinations of the density vary from 5.1 to 5.8.

The Arrangement of the Atoms

Laue photographs of the two substances showed holohedral cubic symmetry, so the arrangement must be that of one of the space groups isomorphous with the point groups T_d , O, and O_h . No spots were produced by first-order reflections from planes having one or two even indices, such as (521) and (421). Also, no spots were produced by first, second, or third order reflections from planes having one index zero and only one index odd, such as (320) and (100). Assuming all the arsenic or antimony atoms, and likewise all the oxygen atoms, to be equivalent, the only possible arrangement which will satisfy the above conditions and permit first-order reflections from planes having all odd indices is the following, derivable from the space-group O_h^a :

⁴ Muir and Hutchinson, J. Chem. Soc., 60, 143 (1889), and Doelter's "Handbuch der Mineralchemie," Steinkopff, Dresden and Leipzig, 1918, vol. 3, pt. 1, p. 757.

⁵ Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Inst. Washington, Pub., 318, 144 (1922).

As or Sb atoms at:

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uuu; \frac{1}{2}+u, \frac{1}{2}+u, u; \frac{1}{2}+u, u, \frac{1}{2}+u; u, \frac{1}{2}+u; \frac{1}{2
                      u\bar{u}\bar{u}; \frac{1}{2}+u, \frac{1}{2}-u, \bar{u}; \frac{1}{2}+u, \bar{u}, \frac{1}{2}-u; u, \frac{1}{2}-u, \frac{1}{2}-u;
                      \bar{u}u\bar{u}; \frac{1}{2}-u, \frac{1}{2}+u, \bar{u}; \frac{1}{2}-u, u, \frac{1}{2}-u; \bar{u}, \frac{1}{2}+u, \frac{1}{2}-u;
                      \bar{u}\bar{u}u; \frac{1}{2}-u, \frac{1}{2}-u, u; \frac{1}{2}-u, \bar{u}, \frac{1}{2}+u; \bar{u}, \frac{1}{2}-u, \frac{1}{2}+u;
                        \frac{1}{4} - u, \frac{1}{4} - u, \frac{1}{4} - u; \frac{3}{4} - u, \frac{3}{4} - u, \frac{1}{4} - u; \frac{3}{4} - u, \frac{1}{4} - u, \frac{3}{4} - u; \frac{1}{4} - u, \frac{3}{4} - u; \frac{3}{4} - u; \frac{3}{4} - u;
                        \frac{1}{4} - u, \frac{1}{4} + u, \frac{1}{4} + u; \frac{3}{4} - u, \frac{3}{4} + u, \frac{1}{4} + u; \frac{3}{4} - u, \frac{1}{4} + u, \frac{3}{4} + u; \frac{1}{4} - u, \frac{3}{4} + u, \frac{3}{4} + u;
                        \frac{1}{4}+u, \frac{1}{4}-u, \frac{1}{4}+u; \frac{3}{4}+u, \frac{3}{4}-u, \frac{1}{4}+u; \frac{3}{4}+u, \frac{1}{4}-u, \frac{3}{4}+u; \frac{1}{4}+u, \frac{3}{4}-u, \frac{3}{4}+u;
                        \frac{1}{4}+u, \frac{1}{4}+u, \frac{1}{4}-u; \frac{3}{4}+u, \frac{3}{4}+u, \frac{1}{4}-u; \frac{3}{4}+u, \frac{1}{4}+u, \frac{3}{4}-u; \frac{1}{4}+u, \frac{3}{4}+u, \frac{3}{4}-u.
O atoms at:
                      v00; \frac{1}{2} + v, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2} + v, 0; v_{\frac{1}{2}\frac{1}{2}};
                      \bar{v}00; \frac{1}{2} - v, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2} - v, 0; \bar{v}, \frac{1}{2};
                        0v0; \frac{1}{2}, 0, \frac{1}{2} + v; \frac{1}{2} + v, 0, \frac{1}{2}; \frac{1}{2}v\frac{1}{2};
                        0\bar{v}0; \frac{1}{2}, 0, \frac{1}{2} - v; \frac{1}{2} - v, 0, \frac{1}{2}; \frac{1}{2}\bar{v}\frac{1}{2};
                         00v; 0, \frac{1}{2} + v, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2} + v; \frac{1}{2}, \frac{1}{2}v;
                        00\overline{v}; 0,\frac{1}{2}-v,\frac{1}{2}; 0,\frac{1}{2},\frac{1}{2}-v; \frac{1}{2}\overline{v};
                         \frac{1}{4} + v, \frac{1}{4}, \frac{1}{4}; \frac{3}{4} + v, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4} + v, \frac{1}{4}; \frac{1}{4} + v, \frac{3}{4}, \frac{3}{4};
                          \frac{1}{4} - v, \frac{1}{4}, \frac{1}{4}; \frac{3}{4} - v, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4} - v, \frac{1}{4}; \frac{1}{4} - v, \frac{3}{4}, \frac{3}{4};
                          \frac{1}{4}, \frac{1}{4} + v, \frac{1}{4}; \frac{3}{4}, \frac{1}{4}, \frac{3}{4} + v; \frac{3}{4} + v, \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4} + v, \frac{3}{4};
                          \frac{1}{4}, \frac{1}{4} - v, \frac{1}{4}; \frac{3}{4}, \frac{1}{4}, \frac{3}{4} - v; \frac{3}{4} - v, \frac{1}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4} - v, \frac{3}{4};
                          \frac{1}{4}, \frac{1}{4}, \frac{1}{4} + v; \frac{1}{4}, \frac{3}{4} + v, \frac{3}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4} + v; \frac{3}{4}, \frac{3}{4}, \frac{1}{4} + v;
                          \frac{1}{4}, \frac{1}{4}, \frac{1}{4} - v; \frac{1}{4}, \frac{3}{4} - v; \frac{3}{4}, \frac{3}{4}, \frac{1}{4} - v; \frac{3}{4}, \frac{3}{4}, \frac{1}{4} - v;
```

The Laue Photograph of Arsenious Oxide

The data from a Laue photograph of arsenious oxide, taken with the beam inclined about 2° to a trigonal axis, are given in the first 4 columns of Table III. The attempt has been made to make this table complete by including all forms below a certain complexity (d/n = 0.78 Å.) which could possibly have reflected X-rays onto the photographic plate as pure first-order or pure second-order reflections. First-order reflections from planes having an even index are not tabulated, for none was observed, and with the arrangement given above the structure factor S is identically zero for them. A few reflections involving wave lengths near and below 0.30 Å. were also omitted, since the data are not useful. In the table, d denotes the interplanar distance expressed in Ångstrom units and n the order of reflection. The wave lengths of the X-rays are expressed in Ångstrom units.

Assuming that the reflecting powers of the atoms are proportional to their atomic numbers, the structure factor was calculated in the usual way for each of the planes listed in Table III for a considerable region near u=0.9 and v=0.2. The calculated structure factors agree best with the data when u is 0.895 and v is 0.21. The value of u cannot be changed more than 0.005 without destroying the agreement between calculated structure factors and observed intensities. Because of the comparatively small reflecting power of oxygen, however, the value of v may be changed as much as 0.02 without seriously affecting the agree-

ment. Values of u and v differing markedly from 0.9 and 0.2, respectively, were found by trial to be inconsistent with the data.

Table III

Laue Photographic Data for Arsenious Oxide

	LAUE PHOTO	RAPHIC	DATA FOR	Arsenious	OXIDE	*
	THOR THOSE				ted structure = 0.895, v =	factors for
	d/n	Wave length	Estimated intensity	S_{AB}	S _{0x}	S
n(hkl)		0.35	0.4	20	6	26
$(5\overline{3}\overline{1})$	1.87	.37	.1	- 2	- 5	- 7
$(3\overline{5}3)$	1.69		2.0	69	24	93
$(1\overline{5}5)$	1.55	.34		0	0	0
$2(03\overline{2})$	1.53	.41	0.0	- 22	0	- 22
$2(2\overline{3}2)$	1.34	.42	.2	- 22 15	3	18
$(71\overline{5})$	1.28	.45	.2	- 50	0	- 50
$2(\overline{124})$	1.21	.38	.6	- 30 - 10	10	Õ
$(5\overline{7}5)$	1.11	.43	.0		0	0
$2(\overline{3}04)$	1.11	.32	.0	0	-22	- 34
$2(41\overline{3})$	1.08	.43	.03	- 12		50
(737)	1.07	.40	.7	80	-30	
$(\overline{15}9)$	1.07	.43	.5	- 69	22	- 47
$2(5\overline{21})$	1.01	.41	.15	- 27	8	- 19
(577)	1.00	.46	.0	13	-11	2
$2(\overline{3}05)$	0.95	.42	.5	- 84	28	- 56
$2(3\overline{4}3)$.95	.41	.15	32	- 9	23
$(\overline{3}\cdot 11\cdot \overline{3})$.94	.42	.2	71	-20	51
(937)	.94	.41	.1	- 25	-10	– 35
$(\overline{5}\cdot 11\cdot \overline{1})$.91	.41	.1	- 47	- 9	- 56
$2(43\overline{4})$.86	.42	.2	- 67	0	- 67
$2(\overline{1}6\overline{2})$.86	.43		60	0	60
$2(1\overline{4}5)$.85	.42	.0	16	- 8	8
(1.7.11)	.85	.43		42	-12	30
(3.11.7)	.83	.45		- 67	-23	- 90
(977)	.83	.38		31	-13	18
$2(2\overline{4}5)$.82	.47		- 16	0	- 16
$(\overline{3}\cdot 13\cdot \overline{3})$.81	.45			-17	- 84
(599)	.81	.38			28	- 49
$(13\cdot\overline{1}\cdot\overline{5})$.79	.43		53	12	65
$2(35\overline{4})$.78	.47			5	- 40
$2(334)$ $2(1\overline{4}6)$.76	.41			0	-105
	.75	.45		27	-26	2
$2(7\overline{12})$.73	.43			15	- 28
$(5.\overline{9}\cdot11)$.73	.47			-20	40
(13.3.7)		.37		1.00	0	28
2(454)	.73	.43		. 26 86	30	116
2(370)	.73	.48			0	79
$2(36\overline{4})$.71				-20	47
$(15\cdot\overline{5}\cdot\overline{1})$.70	.4			-20 -13	40
(11.9.9)	.66	.3		The second of the second	-13 36	141
$2(2\overline{5}7)$.63	.30			0	95
$2(\overline{4}18)$.61	.4:				103
$(15\cdot 5\cdot \overline{9})$.61	.4	Told with the			
	. Profit i⊒s absolved in a d	State of the State of the	er ale tradition in the	No. 1 To a Control of the Au		3 4 41

The structure factor can be separated into two parts, S_{As} due to the arsenic atoms alone, and S_{Ox} due to the oxygen atoms alone, so that $S = S_{As}$ +

 S_{Ox} . This separation is made in the tables, in order that it may be seen how the final value of S would change if the reflecting powers of the atoms were not considered to be proportional to their atomic numbers. The intensity of reflection of any plane is assumed to be some function of d/n, multiplied by S^2 .

The Laue Photograph of Antimonous Oxide

The Laue data for antimonous oxide are given in Table IV. It is seen that the intensity data are satisfied when u=0.885 and v=0.23. The same limitations apply to the values of the parameters that held in the case of arsenious oxide. With either substance the particular values $u=\frac{7}{8}$ and $v=\frac{1}{4}$ will not satisfy the data. Since antimony shows a critical absorption at 0.405 Å., reflections of wave lengths near or below this value have not in general been included, for they are extremely weak.

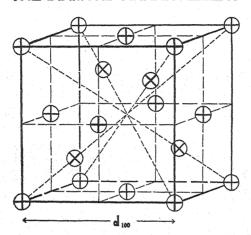
TABLE IV
LAUE PHOTOGRAPHIC DATA FOR ANTIMONOUS OXIDE

148	OE I HOIOG	KAPHIC I	DAIA FOR I	Cal	culated struc	ture factors
		Wave	Estimated		u = 0.885, v	=0.23
n(hkl)	d/n	length	intensity	S_{Sb}	S_{0x}	S
$(3\overline{5}3)$	1.70	0.38	0.0	4	- 2	2
$(1\overline{5}5)$	1.56	.35	.15	68	15	83
$2(3\overline{2}0)$	1.54	.49	.0	0	. 0	0
$2(2\overline{3}2)$	1.35	.43	.1	- 12	0	- 12
$(71\overline{5})$	1.29	.42	.1	8	- 1	7
$(5\overline{7}5)$	1.12	.44	.1	11	5	16
$(3\overline{7}7)$	1.08	.43	1.0	98	-22	76
$(\overline{15}9)$	1.08	.44	1.0	- 86	18	- 68
$(75\overline{7})$	1.00	.44	0.3	44	-11	. 33
$2(\overline{3}05)$	0.95	.45	.15	-45	- 1	- 46
$2(3\overline{4}3)$.95	.42	.1	25	-15	10
$(11\cdot\overline{3}\cdot\overline{3})$.94	.43	.8	96	-19	77
$2(6\overline{21})$.87	.45	.1	35	0	35
(1.7.11)	.85	.44	.5	88	-18	70
(11.3.7)	.83	.44	.6	-111	-24	-135
$2(\overline{4}52)$.83	.43	.01	- 20	0	- 20
$(\overline{3}\cdot 13\cdot \overline{3})$.81	.44	.15	— 50	3	- 47
$(13\cdot\overline{5}\cdot\overline{1})$.80	.45	.3	100	19	119
$2(35\overline{4})$.79	.45	.05	- 39	- 8	- 47
(1.7.13)	.75	.46	.01	- 40	4	- 36
$(15\cdot\overline{5}\cdot\overline{1})$.70	.44	.05	59	- 3	56
$2(4\overline{5}5)$.69	.42	.05	63	- 1	- 62
(1.7.15)	.67	.47	.1	- 96	-18	-114
$(13\overline{9}.5)$.67	.43	.15	128	28	156
(15.3.7)	.66	.46	.1	118	-24	94
$2(4\overline{5}6)$.63	.45	.01	- 56	0	- 56
$(17\cdot\overline{5}\cdot\overline{1})$.63	.43	.05	-107	18	- 89
2(148)	.62	.44	.05	84	0	84
2(457)	.59	.46	.05	83	7	- 76
$(17\overline{\cdot 9}.5)$.56	.43	.01	-127	26	101
	医抗性性性 化烷化烷基酚烷					

Conclusions Concerning the Crystal Structure

The structure is represented diagrammatically by Fig. 1. It consists of As_4O_6 or Sb_4O_6 groups arranged in the same way as the carbon atoms in the diamond, 6 each group corresponding to one carbon atom. It will be seen that the atoms in each As_4O_6 or Sb_4O_6 group are related among themselves in a way different from that in which they are related to the atoms of other groups, and that the groups themselves are separated by distances

THE DIAMOND ARRANGEMENT



To represent As4O6 and Sb4O6,

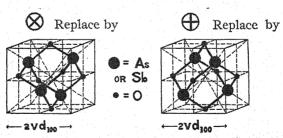


Fig. 1.—The arrangement of the atoms in As_4O_6 , and Sb_4O_6 . For As_4O_6 , $d_{100}=11.06$, u=0.895 and v=0.21; for Sb_4O_6 , $d_{100}=11.14$, u=0.885 and v=0.23

considerably greater than the distances between the atoms in any group. For example, the shortest distance between an arsenic and an oxygen atom within the same group is 2.01 Å., while the shortest distance between an arsenic atom and the nearest oxygen atom in a neighboring group is 2.78 Å. The corresponding distances in antimonous oxide are 2.22 Å. and 2.61 Å., respectively. Hence, in the solid as well as in the gaseous state, molecules of As_4O_6 and Sb_4O_6 may be considered to exist.

⁶ W. H. and W. L. Bragg, Proc. Roy. Soc., London, 89A, 277 (1913).

This determination of the arsenic to oxygen distance is, so far as the writer is aware, the only basis for an experimental value of the arsenic radius. Taking the oxygen radius as $0.65 \, \text{Å}$, the arsenic radius is $1.36 \, \text{Å}$. The radius of antimony is found in the same way to be $1.57 \, \text{Å}$.

The arrangement of the atoms within the molecule is the same as that of the carbon and nitrogen atoms in hexamethylenetetramine, $C_6N_4H_{12}$, as determined by Dickinson and Raymond.⁷ The considerations concerning the tetrahedral angles that hold for the latter compound apply also to arsenious and antimonous oxides.

Summary

The crystal structures of arsenious and antimonous oxides have been determined by means of Laue photographs and spectral photographs. These crystals may be regarded as composed of $\mathrm{As_4O_6}$ and $\mathrm{Sb_4O_6}$ molecules having a diamond arrangement, each molecule corresponding to 1 carbon atom. See Fig. 1. The arrangements are derived from the space group $\mathrm{O_h^7}$. The sizes of the unit cubes containing 8 molecules of $\mathrm{As_4O_6}$ or $\mathrm{Sb_4O_6}$ are 11.06 Å. for arsenious oxide and 11.14 Å. for antimonous oxide. The shortest distance between arsenic and oxygen atoms is 2.01 Å., and between antimony and oxygen atoms is 2.22 Å.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTROCHEMISTRY, UNIVERSITY OF LIVERPOOL]

THE EFFECT OF SUCROSE ON THE ACTIVITIES OF CERTAIN IONS

By J. W. CORRAN Received March 26, 1923

Experiments with Potassium Chloride

With the object of investigating the mechanism of chemical change, a method has been adopted in this Laboratory in the case of reactions in aqueous solutions which consists in making use of an artifice, namely, the replacement of various amounts of the water by sucrose, such replacement being attended by measurable alterations in viscosity on the one hand, and in the activities of the participating individuals, (molecules and ions), on the other. On the basis of this simultaneous alteration, information can be obtained regarding the nature of the process taking place in presence of the sucrose. In the first instance, it is necessary to obtain, by direct experiment, a value for only the actual change in activity produced by the sucrose, in order to apply the method. At the same time, the question naturally arises as to the mechanism of the alteration in activity itself, as in the case of an ion, and in a previous communica-

⁷ Dickinson and Raymond, This Journal, 45, 22 (1923).

tion¹ the attempt was made to account for the alteration in the activity of the chloride ion in terms of the available water present. In the paper referred to, the activities of the chloride ion, in the presence of various amounts of sucrose, were computed from measurements of the electromotive force of cells with transport, using silver-silver chloride electrodes. The expression for the e.m.f.'s of such cells is

$$E = 2n_{\rm K} \frac{RT}{F} \log \frac{{\rm Cl_{I}}}{{\rm Cl_{II}}}$$

where $\mathrm{Cl_I}$ and $\mathrm{Cl_{II}}$ are the activities of the chloride ion in the solutions and n_K represents the transport number of the potassium ion. It was assumed that in solutions of potassium chloride, the activities of the two ions were equal, even in the presence of sucrose (an extension of the Mac-Innes² postulate which states that in aqueous solutions of potassium chloride the activities of the potassium and chloride ions are equal). Further, it was assumed that the transport number of the potassium ion retained the same value in solutions containing sucrose as in aqueous solutions. It was shown that the general nature of the results obtained justified these two assumptions.

The most important inference drawn from the results obtained by means of the cell with transport was that the potassium and chloride ions are soluble in the water of hydration of sucrose, the activities of the ions being calculable with a fair degree of accuracy on this basis, activity being regarded at the same time as a concentration expressed in terms of available solvent. When the concentration of sucrose was large, however, the observed activities tended to become slightly less than those calculated on the assumption that increase in activity was due to the decrease in the total amount of water present in the solution, owing to the sucrose. These differences may have been due to experimental error. There was also a possibility that the transport number of the potassium ion had slightly, but sensibly, changed and, hence, had influenced the values of the activities calculated from the observed e.m.f.'s. This being the position it was deemed advisable to verify the results already obtained by means of the corresponding cell without transport, namely, Ag | AgCl | KCl | $K_{\rm x}$ Hg |

KCl and sucrose AgCl Ag. The e.m.f. of this type of cell is given by the

expression, $E = \frac{2RT}{F} \cdot \log \frac{\text{Cl}_{\text{I}}}{\text{Cl}_{\text{II}}}$, on the assumption that the activities of the potassium and chloride ions are equal. Any pronounced changes in the transport number of the potassium ion should be demonstrated by a comparison of the results obtained by means of the two types of cell.

² MacInnes, ibid., 41, 1086 (1919).

¹ Corran and Lewis, This Journal, 44, 1673 (1922).

Experimental Part

The electrical instruments and silver-silver chloride electrodes were as described in a previous paper. A type of flowing amalgam electrode, identical with that used by MacInnes and Parker, was employed. The precautions adopted by these authors were followed, and their statements were completely verified by the present investigation. The potassium amalgam was also prepared according to their recommendations and, provided that air was excluded, it was found to be very satisfactory. The amalgam was kept under pure, dry hydrogen.

All measurements of the cell were carried out at 25° . The concentrations of potassium chloride used were 0.5~N and 0.1~N, respectively, (moles per liter of solution) and the sucrose was introduced into the decinormal solution of potassium chloride.

The expression from which the activities were calculated was the following, $E=2\times0.059\times\log\frac{0.324}{a_{\text{Clo.1}}}$, where 0.324 is the activity of the chloride ion in 0.5 N potassium chloride and $a_{\text{Clo.1}}$ is that in the decinormal solution in the presence of sucrose. Table I contains the values of the observed e.m.f.'s and also the activities calculated from these values by means of the above expression. The values marked with an asterisk were interpolated by a graphical method.

per 100 cc.		-				
of solution G.	Volts	—E.m.f. obs.—— Volts	Volts	Av. e.m.f.	a _{Clo.1}	
0	0.0738	0.0741	0.0740	0.0740	0.0764	
10	.0706				.0817	
20	.0674				.0870	
30	.0642			.0642	.0925	
40	.0600	.0598	.0602	.0600	. 1005	
50	.0556			.0556	.1095	
60	.0510	; .		.0510	.1198	
70	.0454	.0456		.0455	.1333	

In Table II are shown the activities of the chloride ion in decinormal solutions of potassium chloride in the presence of sucrose, calculated from the e.m.f.'s of the cells with and without transport, respectively. In the last column are given the "theoretical" activities, 4 a_2 , of this ion, calculated in terms of total water, on the basis that the activity is a corrected concentration and that sucrose, beyond the fact that it displaces a certain amount of water, is otherwise inert.

- 3 MacInnes and Parker, This Journal, 37, 1445 (1915).
- ⁴ In order to determine the values of the "theoretical" activities in terms of total water, the compositions of the solutions by weight were found and the concentrations of potassium chloride were expressed as moles per 1000 g. of total water (see the first 3 columns of Table II). The activity coefficients corresponding to these concentrations were obtained from the data of Noyes and MacInnes [This Journal, 42, 239 (1920)]. The product of these concentrations and the corresponding activity coefficients gave the "theoretical" activities shown in Table II.

Table II

Comparison of Results Obtained by Means of Cells with and without Transport,

Respectively

per liter	Total water per liter o	f 1000 g.	Cell with to	ransport Relative	Without tr	ansport Relative	Theor activ	etical ities Relative
of solution G.	G.	of water Moles	acta-1	activity	a Clo-1	activity	a_2	activity
0	995.05	0.1005	0.0760	1.00	0.0764	1.00	0.0749	1.00
100	933.0	.1072	.0809	1.06	.0817	1.07	.0795	1.06
200	871.6	.1147	.0865	1.14	.0870	1.14	.0850	1.135
300	809.5	. 1235	.0921	1.21	.0925	1.21	.0909	1.21
400	748.0	. 1337	.0993	1.31	.1005	1.31	.0981	1.31
500	681.7	.1467	.1070	1.40	.1095	1.43	.1068	1.43
600	618.8	.1616	. 1158	1.52	.1198	1.57	.1168	1.56
700	554.1	.1805	.1258	1.66	.1333	1.74	.1289	1.72

It was shown previously¹ that the activities obtained by means of a consideration of the cell with transport showed an increase parallel with those of a_2 ("theoretical" activities) calculated in terms of total water, except in the case of solutions containing 60 and 70% of sucrose. In these cases, the observed activities were found to be slightly less than those calculated. This slight divergence does not appear when activities are calculated from the e.m.f.'s of cells without transport. Hence the conclusion that the potassium and chloride ions are soluble in the water of hydration of sucrose is fully substantiated by the results obtained by means of the cell without transport.

The Transport Number (n_K) of the Potassium Ion in the Presence of Sucrose

In Table III are given the ratios of the e.m.f.'s of the two types of cell or, in other words, the values for the transport number of the potassium ion in solutions of potassium chloride, in the presence of sucrose. On account of the fact that the value for $E_{\rm obs.}$, for 70% sucrose (cell with transport), namely, 0.0240, is the mean of several values which exhibited among themselves a variation of 1 mv., the value of the transport number is also an average value, between the limits 0.514 and 0.530, which is a considerable variation for a transport number. This example demonstrates the effect of a comparatively small error in the observed e.m.f. on the value of the transport number obtained. However, the results tend to show that the transport number of the potassium ion does increase slightly in 60 and 70% solutions, but remains practically constant up to 50% sucrose. That is, the assumption made in the previous paper, regarding the constancy of the transport number of the potassium ion, is approximately justified.

It is a somewhat striking conclusion that, up to 50% sucrose solutions, the transport number of the potassium ion, and also of the chloride ion, should hardly alter, even though the viscosity increases 7-fold.

Table III
Transport Numbers of Potassium Ion

Sucrose	Viscosity of solution	$E_{ m obs}.$ (cell with transport)	$E_{ m obs}$. (cell without transport)	Transport no. of potassium
0	1.00	0.0368	0.0740	0.497
10	1.32	.0352	.0706	.498
20	1.80	.0335	.0674	.497
30	2.63	.0319	.0642	. 497
40	4.09	.0300	.0600	. 500
50	6.86	.0281	. 0556	. 505
60	12.77	.0261	.0510	.511
70	25.93	.0240	.0455	. 527

Discussion of Results

Harned⁵ has published results which serve to verify the conclusion arrived at during the present investigation regarding the solubility of the chloride ion in the water of hydration of sucrose. He considered cells of the following types: (1) $H_2 \mid \text{MeCl}(c)$ in $\text{HCl}(0.1) \mid \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$; (2) $H_2 \mid \text{MeCl}(c)$ in $\text{HCl}(0.1) \mid \text{HCl}(0.1) \mid \text{Hc}_2$, where Me represented potassium, sodium or lithium. The concentration of hydrochloric acid in each case was 0.1 M, while that of the alkali chloride was denoted by c. Hence the total chloride concentration was (c + 0.1).

The free energy changes in these 2 cells are given by the following expressions.

$$\begin{split} \text{Cell 1} & \quad -(\Delta F)_1 = F(E_0(1) - E(1)) \\ & = RT \log \frac{a_{\text{H}_8} \cdot a_{\text{Cl}_{(e+0\cdot 1)}}}{a_{\text{H}_0\cdot 1} \cdot a_{\text{Cl}_{0\cdot 1}}} \\ \text{Cell 2} & \quad -(\Delta F)_2 = FE_2 = RT \log \frac{a_{\text{H}_8}}{a_{\text{H}_6,1}} \end{aligned}$$

where $-(\Delta F)$ denotes decrease in free energy, E_0 the e.m.f. of the cell when c is zero, and E that when there is salt present; $a_{\rm H_s}$ denotes the activity of the hydrogen ion in the presence of salt. The value of the e.m.f. of Cell 2 was determined indirectly, in order that liquid-liquid potential differences should not be involved. If we subtract the value of Cell 2 from that of Cell 1, the following expression is obtained.

$$E_{\rm 0}(1) - E(1) - E(2) = \frac{RT}{F} \log \frac{a_{\rm Cl_{\rm 0.0+0.1}}}{a_{\rm Cl_{\rm 0.1}}}$$

In Table IV is given a summary of the results of Harned for the values of $\frac{RT}{F}$ log $\frac{a_{\text{Cl}}_{(e+0\cdot 1)}}{a_{\text{Cl}_{0\cdot 1}}}$, in the cases of potassium, sodium and lithium chlorides,

respectively. The value of the logarithmic expression for the same value of c is practically the same in the cases of all 3 salts. If the chloride ion were insoluble in the water of hydration of the accompanying cation, one would

⁵ Harned, This Journal, 42, 1808 (1920).

expect that the value of the expression would be greatest in the case of lithium chloride solutions and least in those of potassium chloride, since, according to Washburn, 6 the lithium ion is much more heavily hydrated than the sodium ion, which in turn possesses a greater degree of hydration

Table IV Harned's Results

$$\frac{RT}{F} \log \frac{a_{\text{Clo-1}}}{a_{\text{Clo-1}}} \begin{cases} \text{KCl...} & 0.2000 & 0.5000 & 1.000 & 2.000 & 3.000 \\ 0.0244 & 0.0404 & 0.0554 & 0.0724 & 0.0834 \\ \text{NaCl...} & .0241 & .0401 & .0548 & .0712 & .0821 \\ \text{LiCl...} & .0244 & .0400 & .0555 & .0718 & ... \end{cases}$$

than the potassium ion. In 2.00~M solutions of these salts the different "effective" concentrations of the chloride ion which would be thus caused, if this ion were insoluble in the water of the hydration of the cations, would certainly affect the value of $a_{\text{Cl}\,(c+0.1)}$ in such a way that it would be much greater in the solution of lithium chloride than in that of potassium chloride. But this is not so, as the table shows that the logarithmic expression is very slightly greater in the case of potassium chloride, probably due to slight experimental error. Hence, one can only conclude that the chloride ion is soluble in the water of hydration of the accompanying cations, a conclusion which is the analog of that arrived at in the present investigation, for the case of sucrose.

Experiments with Barium Chloride

The principle of the method employed for the measurement of the activities of the barium ion in the presence of sucrose is essentially the same as that employed in the case of the potassium and chloride ions. The cell without transport was used, namely, Ag | AgCl | BaCl₂ | Ba_xHg | Ba-

Cl₂ and sucrose AgCl Ag. The e.m.f. of this cell, in which solutions of a uni-bivalent electrolyte are used, is given by the expression

$$E = \frac{3RT}{2F} \log_{\bullet} \sqrt[3]{\frac{\text{Ba}_{\text{I}}.\text{Cl}_{\text{I}}^2}{\text{Ba}_{\text{II}}.\text{Cl}_{\text{II}}^2}}$$

where $Ba_{\rm I}$ and $Cl_{\rm I}$ are the activities of the barium and chloride ions, respectively, in the first solution and $Ba_{\rm II}$ and $Cl_{\rm II}$ are those in the second solution. The value of $\sqrt[3]{Ba.Cl^2}$ is the mean activity of the ions or, in other words, the activity of the barium chloride. It is evident that, knowing the mean activity in the first solution, a measurement of e.m.f. enables one to calculate the value in the second solution.

In order to obtain the individual barium-ion activities from a knowledge of the mean activities, it can no longer be assumed, as in the case of univalent chlorides, that in solutions of the same equivalent concentration the activities of the chloride ion in a uni-univalent and a uni-bivalent

⁶ Washburn, This Journal, 31, 322 (1909).

chloride, respectively, are the same. Such an assumption would be in contradiction to the results of Lewis and Randall⁷ and Brönsted.⁸ that the activity coefficient of an ion is a function of the total ion concentration or, in the words of Lewis and Randall, of the "ionic strength" of the solution. However, it is possible to calculate indirectly, on the basis of previous conclusions, the relative increase in the barium-ion activity caused by the presence of sucrose. It is known that the chloride-ion activity. in the presence of sucrose, is inversely proportional to the total amount of water in a given volume of solution. Applying this result to the case of barium chloride solutions, it is evident that the relative activities of the chloride ion can be calculated from a knowledge of the compositions by weight of the solutions. In addition, measurements of the e.m.f.'s of the above cell will furnish a means for the calculation of the relative activities of barium chloride, that is, the mean activities of the ions in the presence of various amounts of sucrose. From the values obtained for barium chloride and chloride ion, respectively, it is an easy matter to calculate the relative activities of the barium ion alone; they are the cubes of the relative activities of the barium chloride divided by the squares of those of the chloride ion itself. From the values thus obtained for the barium ion, information regarding its solubility or insolubility in the water of hydration of sucrose can be obtained in a manner similar to that adopted in the case of solutions of potassium chloride.

In order to assign correct values to the activity of the barium ion in the presence of sucrose, the values of the activity coefficients of barium chloride and chloride ion in 0.1 M barium chloride solution in the absence of sucrose, as given by Lewis and Randall⁷ and Harned and Brumbaugh,⁹ respectively, have been employed and the required activity of barium ion has been calculated from them. Using the value so obtained as that of the barium ion when no sucrose was present, the barium-ion activity in the presence of sucrose can be calculated from a knowledge of the relative activities.

Experimental Part

The amalgam was prepared by the electrolysis of a saturated solution of barium hydroxide, using a cathode of pure mercury and a platinum anode. On passing a current of 1.5 amp. (current density about 50 milliamp. per sq. cm.) for about 2 hours while the mercury was constantly stirred, a liquid amalgam was formed containing about 0.1% of barium. This amalgam was separated from the solution and washed several times with small amounts of distilled water. It was then dried in a vacuum, with the help of gentle heat, and finally kept under pure, dry hydrogen.

- 7 Lewis and Randall, This Journal, 43, 1112 (1921).
- ⁸ Brönsted, *ibid.*, **42**, 761 (1920).
- ⁹ Harned and Brumbaugh, *ibid.*, 44, 2729 (1922).

The amalgam, which closely resembled potassium amalgam, acquired a dark film on the surface and decomposed slowly in water, and rapidly in acid solution

The measurements were carried out at 25°, in a manner similar to that used in the case of solutions of potassium chloride, the flowing amalgam electrode being again employed, owing to the reaction between barium and water to form barium hydroxide. The concentrations of barium chloride employed were 0.5 and 0.1 moles per liter of solution, respectively, and into the latter solution were introduced various amounts of sucrose.

It was assumed that, in the expression for the e.m.f. of the cell, namely,

$$E = 0.0885 \log \sqrt[3]{\frac{Ba_{0.5} \cdot Cl^{2}_{0.5}}{Ba_{0.1} \cdot Cl^{2}_{0.1}}}$$

the activity of the barium chloride in $0.1\,M$ solution when no sucrose was present was unity. Thus the values obtained when sucrose was present gave the relative increase in the activity of barium chloride caused by the sucrose. In Table V are shown the results of the e.m.f. measurements, together with the calculated relative activities (or the relative increase in activity), in the cases of 0, 40 and 60% solutions of sucrose.

Sucrose	$E_{ m obs}$	(volts)	Average	Relative mean activity		
%	0.1% amalgam	0.01% amalgam	e.m.f.	√ ³ /Ba.Cl ²		
0	0.0523	0.0526	0.0524	1.00		
40	.0427	. 0426	.0426	1.28		
60	.0348	.0343	.0346	1.59		

Expressing the concentration of barium chloride as moles of salt per 1000 g. of water, the relative concentrations can be calculated, as in the case of potassium chloride, assuming that the concentration of salt when no sucrose is present is unity. These relative "corrected" concentrations $(c_{\text{corr.}})$, in terms of total water, are shown in Col. 3 of Table VI. In the fourth column are shown the observed relative activities.

Table VI Barium-ion Activities

Sucrose per liter of solution G.	Total water per liter of solution G.	corr. (in terms of total water)	Relative mean activities (obs.)	Barium-ion activities a _{Ba}
0	995.6	1.00	1.00	0.029
400	746.0	1.34	1.28	.037
600	615.0	1.62	1.59	.046

The values of $c_{\rm corr.}$ are slightly higher than those of the relative activities, but it must be remembered that, as the concentration increases, the activity coefficient decreases slightly. If we allow for this decrease in the

activity coefficient, the values in Cols. 3 and 4 will agree more closely. Since there are no accurate experimental data expressing the activity coefficient of barium chloride as a function of concentration, no attempt has been made to allow exactly for the slight decrease in activity coefficient.

It is evident from the results shown in the above table, that the increase in the mean activity of the ions of barium chloride, caused by the presence of sucrose, can be accounted for by simply allowing for the decrease in the total amount of water. In other words, since the chloride ion has been shown to be soluble in the water of hydration of sucrose, the same conclusion is arrived at in connection with barium ion. Therefore, the values shown in Col. 4 represent not only the relative mean activities of the barium and chloride ions, but also the relative activities of the individual barium and chloride ions, respectively. Hence, by assigning the value 0.029 to the activity of the barium ion in 0.1 M aqueous solution, the values shown in the last column of Table VI for the actual barium-ion activities, are obtained.

Discussion of Results

Regarding the activity of an ion as the product of the concentration and the activity coefficient, the significance of the foregoing treatment lies in the fact that it throws considerable light on the mode of expressing concentration. It is clear that the availability or non-availability as solvent of the water of hydration of ions or non-electrolytes is of primary importance. In the cases examined during the present investigation, the chloride, potassium and barium ions are apparently soluble in the water of hydration of sucrose. In addition, it has been shown, from a survey of Harned's results,5 that the chloride ion is soluble in the water of hydration of accompanying cations. On the other hand, Moran and Lewis¹⁰ have shown that the hydrogen ion is apparently insoluble in the water of hydration of sucrose, since the increase in its activity caused by sucrose is not accounted for, even by allowing for the water of hydration. addition, the fact that lithium chloride causes a greater increase in the hydrogen-ion activity of hydrochloric acid than does potassium chloride or sodium chloride, indicates that the hydrogen ion is insoluble in the water of hydration of salts. In view of this, the hypothesis of MacInnes, as extended by Harned, 5 namely, that in solutions of uni-univalent electrolytes of the same concentration and having an ion in common, the activity of the common ion has the same value in every case, is not strictly true. It cannot be true, for example, in the case of strong monobasic acids at the same concentration, for if it were, in view of what has been said, it would follow that the anions must be hydrated to equal extents, a conclusion that is untenable. However, it must be stated that, in view of

¹⁰ Moran and Lewis, J. Chem. Soc., 121, 1613 (1922).

the facts and conclusions mentioned, one is led to the conviction that the hydrogen ion stands alone in the sense that it is insoluble in water of hydration, either of an ion or of an undissociated molecule. If this conviction be true, then Harned's extension of the MacInnes postulate should hold for all ions, except the hydrogen ion. The reason for its lack of generality is suggested to be the solubility or insolubility of an ion in the water of hydration of a secondary solute (either an ion or a non-electrolyte).

The author wishes to express his thanks to Professor W. C. M. Lewis, under whose direction the above work has been carried out, and also to the Department of Scientific and Industrial Research of the British Government for a grant which has enabled the research to be performed.

Summary

- 1. By means of measurements of the e.m.f.'s of potassium chloride concentration cells without transport, containing sucrose, the conclusion arrived at in a previous paper that the potassium and chloride ions are soluble in water of hydration of sucrose has been verified.
- 2. It has been shown that whereas the transport number of the potassium ion in sucrose solutions remains constant up to 50% sucrose concentration, it appears to increase slightly in 60 and 70% solutions.
- 3. From a survey of Harned's results, it has been shown that the chloride ion is soluble in the water of hydration of accompanying cations. This conclusion is, therefore, analogous to that arrived at in connection with sucrose.
- 4. Measurements of the mean activities of barium chloride, in the presence of sucrose, by means of the cell without transport, have shown that the barium ion, as well as the potassium and chloride ions, is soluble in the water of hydration of sucrose.
- 5. Since the solubility or insolubility of an ion in water of hydration is of primary importance in determining its true concentration, in terms of available water, Harned's extension to any ion of the MacInnes postulate regarding the independent activity of the chloride ion in solutions of univalent chlorides of the same concentration, is only valid for those ions which are soluble in the water of hydration of secondary solutes (either ions or non-electrolytes).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

THE UPPER RANGE OF THE QUARTZ-FIBER MANOMETER

By Albert Sprague Coolidge Received April 9, 1923

As recently pointed out by Carver, the ordinary forms of micromanometer are not suited for use with organic vapors, either because they demand that the gases whose pressures are being measured shall obey the perfect gas laws, which these vapors do not, or else because they involve the use of hot wires, etc., which might decompose them. Carver solves the problem with the aid of a very elaborate optical-lever mercury manometer. However, it would seem that a much simpler and equally satisfactory solution is offered by the quartz-fiber manometer of Haber and Kerschbaum.²

This instrument, as originally described, consists of a moderately thin quartz fiber sealed at the top into a glass bulb. By gently tapping the bulb, the fiber is set swinging, and the amplitude of its vibration can be determined at any instant with the help of a suitable telescope with micrometer eye piece. This amplitude will decrease with time, at a rate depending upon various factors, but constant under given conditions.

Let $\frac{-dA}{Adt} = C$, the damping constant, where A is the amplitude. Then, by a simple integration, it follows that

$$C = 1/T \ln A_1/A_2 \tag{1}$$

where T is the time (measured by a stopwatch) which elapses while the amplitude decreases from A_1 to A_2 .

Three cases now arise. If the tube is completely vacuous, no damping will occur except that due to the inelasticity of the quartz itself; let this be represented by C=a, where a depends only on the dimensions of the fiber and its temperature. If, however, gas is present, but at such low pressure that the mean molecular free path is large compared to the diameter of the fiber, additional damping will occur, proportionally to the pressure and to the square root of the molecular weight, so that

$$C = a + bp\sqrt{M} \tag{2}$$

where b likewise depends only on the dimensions and temperature of the instrument. Finally, with increasing pressure, the mean free path becomes comparable to or smaller than the diameter of the fiber and Equation 2 ceases to hold; instead, C increases more and more slowly with increasing pressure, and soon reaches a limiting value unchanged by further increase in pressure. This limit is proportional to the viscosity of the gas in the tube and is, therefore, different for different gases. In fact, this differ-

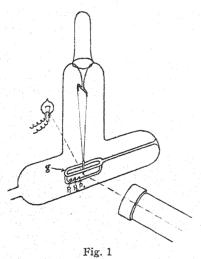
¹ Carver, This Journal, 45, 59 (1923).

² Haber and Kerschbaum, Z. Elektrochem., 20, 296 (1914).

ence in the behavior of gases having different viscosities applies over the whole range just considered.

Obviously the instrument is most useful in its "lower" range, where its behavior follows a simple law, the same for all gases. However, this range extends only up to about 0.01 or 0.02 mm., and leaves a large gap to be filled before the range of the simple mercury manometer is reached. This gap roughly corresponds with the "upper" range of the quartz-fiber gage, that is, the range within which the damping still changes with the pressure, but in a different way with different gases, and can, therefore, be used to measure the pressure only after calibration with another type of gage, with the particular gas in question.

In order to investigate the usefulness of the upper range, two such gages were constructed as shown in Fig. 1. The simple fiber is replaced by a



system of 2 fibers supported at their tops about 1 cm. apart, and having their lower ends joined by a small glass tip. The whole being made out of Pyrex, no difficulty was found in attaching the quartz to the glass, the ends of the fiber being first sealed into small glass armatures, which were in turn attached to the supporting stem. The fibers are about 9 cm. in length and 0.004 cm. in diameter. The tip of Gage B is heavier than that of Gage A. The glass guard ring g serves to limit the travel of the tip and prevents the fiber from ever coming into contact with the walls; it has proved invaluable in preventing breakage. The little glass points $p_1p_2p_3$ in the

figure are used in reading the gage. The cross hairs of the micrometer telescope are set vertically in contact with the images of two of these points $(p_1 \text{ and } p_3 \text{ for a high pressure}; p_1 \text{ and } p_2 \text{ for a low pressure, in order to save time})$, the system set in vibration by suitable shaking, and the time noted during which the extreme position of the tip relapses from coincidence with the cross hair set on p_1 to coincidence with that set on p_3 or p_2 . This time, together with twice the distances of the points from the position of the tip when at rest, is then substituted in Equation 1 to give C. The distances mentioned are found once for all with the aid of the micrometer, and will not change so long as the gage remains mounted in the same position, so that the telescope may be removed and reset as often as desired without introducing additional measurements or computations. During a reading, the top part of the gage is covered with a cap of snow, in order

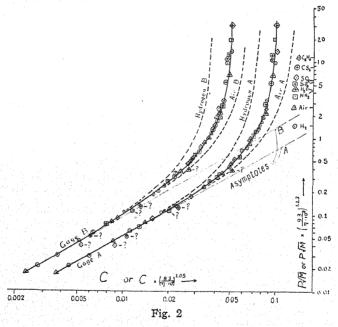
to prevent temperature variations of the constants. It was found that cooling from room temperature to zero reduced the constant a by more than half.

Two advantages accrue from this bifilar construction. First, the system can vibrate only as a whole, and in only one plane, namely, that normal to the line joining the points of support, to which the axis of the telescope should be parallel. In the simple fiber gage, especially with fibers less than 0.01 cm. in diameter, much trouble is experienced from elliptical and harmonic vibrations. Second, the mass of the glass tip serves to decrease the frequency and therewith the rate of damping of the vibrations, so that accurate measurements of the damping time can be made at pressures so high that the simple fiber would be brought to rest in one or two seconds.

The quartz-fiber gages were tested by comparison with McLeod gages, using a variety of gases and vapors. Gold foil was introduced to keep mercury vapor out of the quartz gages. No account was taken of the difference in pressure which must have been caused, at the lowest pressures. by the temperature differences in the system (273° K. at the quartz, about 290° at the McLeod; at very low pressures, where $\Delta p/p = \frac{1}{2} \Delta t/t$ this would amount to about 4%). In interpreting the results it must be kept in mind that the readings on the McLeod gage are not reliable except in the case of the permanent gases. With easily condensible gases and vapors the readings are too low, not because of failure to obey the gas laws during the last stages of compression, but because of adsorption on the walls during the early stages, the adsorbed gas failing to be carried up by the rising mercury. The fraction adsorbed will be the greater, the lower the pressure and the less volatile the vapor in the gage. In an effort to reduce the resulting error by recovering and estimating the adsorbed gas, a McLeod gage was constructed having a main chamber of 500 cc. capacity, and a "capillary" of 15 mm. diameter in which the volume and pressure of the trapped gas could be read after compression (100 times) by a micrometer microscope to 0.05 cc. and 0.01 mm., respectively. the reading was taken, the gas was expelled through an electromagneticallyoperated mercury-sealed glass valve at the top of the capillary, after which the mercury was lowered until it just continued to close the intake-port. Into the vacuum so produced the greater part of the adsorbed gas escaped and was estimated by once more raising the mercury and reading pressure and volume, the amount so found being added to the main portion in calculating the pressure. Even with this correction, it was found that no confidence could be placed in the readings below, say, 0.05 mm. in the case of benzene vapor. On the other hand, the behavior of the quartz gage with this vapor cannot be predicted from Equation 2 much above 0.005 mm., since the mean free path of the benzene molecules is exceptionally short. In the intermediate range an interpretation of the readings with

the quartz gage in terms of pressure can be found, if at all, only indirectly, by analogy from the behavior of permanent gases in the same range.

This behavior is shown by the dashed lines in Fig. 2. The letters A and B refer to the quartz gages A and B, respectively. For the sake of simplicity the observed points are not put down on these curves; furthermore, the hydrogen and air curves for each gage are drawn somewhat closer together than they should be, in order to avoid overlapping. The abscissas are values of C, the damping constant, in reciprocal seconds, while the ordinates represent $p\sqrt{M}$ in millimeters of mercury. A logarithmic scale is used so that a great range may be covered. It will be seen that in the lower range, below about $p\sqrt{M}=0.1$, the curves for both gases coincide, but that above this value they separate, air giving greater damping than hydrogen, in keeping with its higher viscosity. However, the curves



for the two gases have the same shape, and can be brought into coincidence by displacement along their common asymptote. If this relation holds for all gases, and if the required displacement for each gas can be determined by other means, we have evidently a method of interpreting the gage readings with any gas, which does not rely upon the McLeod gage except for a single calibration curve with a permanent gas. A clew as to the amount of displacement required is given by the consideration that the upper limiting values of C should be proportional to the viscosities of the gases. If, therefore, $C \times \eta^{-1}$ or $C \times k\eta^{-1}$ be plotted instead of

C (where η is the viscosity of the gas in question, and k is any constant, the same for all gases) against $p\sqrt{M}$, the upper limits of the curves for all gases will coincide. In order that the lower portions of the curves may coincide, a vertical displacement also is necessary; inspection of the logarithmic graph shows that this should bear to the horizontal displacement the ratio which measures the slope of the asymptote, namely, 1.17. It turns out, however, that the displacement necessary to bring the air and hydrogen curves together is 5% greater than that calculated from the viscosities given in Landolt Börnstein "Tabellen" by the same reasoning. We shall therefore take, as our displaced variables, (arbitrarily setting $k = (93 \times 10^{-6})^{1.05}$), $C \times \left(\frac{93}{\eta \times 10^6}\right)^{1.05}$ for abscissa, and $p\sqrt{M} \times \left(\frac{93}{\eta \times 10^6}\right)^{1.23}$

These variables are plotted in Fig. 2. It is evident that the points for hydrogen and for air actually lie on the same curve within the errors of measurement. (The probable error seems to be about 1% except in the highest range, where it increases because of the smallness of the time intervals measured.) The entire hydrogen curve can, therefore, be derived from the air curve (or *vice versa*) with the aid of knowledge of the viscosity of the two gases, or by a single measurement at a relatively high pressure, in order to determine the displacement required. This latter method, of course, is tantamount to determining the relative viscosity of hydrogen. It is reasonable to hope that in the same way curves for other gases and vapors can be derived, without reliance on the McLeod gage except for one orientating measurement at a relatively high pressure; in the orientating measurements slight errors in the McLeod gage would be unimportant, as C is here almost independent of $p\sqrt{M}$.

This hope appears to be justified. In Fig. 2 are collected observations on 6 additional gases and vapors, having a wide range of viscosities, molecular weights, and volatilities. The viscosities (η_c), calculated from the necessary displacements of the points, are listed in Table I, together with those (η_1) given in Landolt, and the molecular weights.

TABLE I

COMPTON AND MOTHER IN WINTERING ON CACHE

	V 12CO2LLI	S AND MO	LECULAR WEIGI	AIS OF GASES		
Gas	$\eta_c imes 10^{\circ}$	$\eta_1 imes 10_8~M$	Gas	$\eta_c imes 10^6$	$\eta_1 imes 10^6$	M
C ₆ H ₆	71	70.9 78	OS_2	93	92.4	76
H_2	[87]	87.0 2.	02 SO ₂	117	122.5	64
H_2O	93	90.4 18	SiF ₄	147		104.3
NH ₃	93	95.7 17	Air	[175]	175.0	29

In Fig. 2, the symbols used to distinguish the different gases are shown at the right, at positions on the scale of ordinates corresponding to actual pressures of 1 mm. All points lie on the same curves except the 10 points marked "?," which lie too low; but this is exactly what we should

expect, because the McLeod gage reads too low at low pressures, especially with slightly volatile vapors such as those of benzene and water. It will be noticed that these vapors begin to deviate at higher pressures than the others which are more volatile. We may, therefore, safely conclude that the solid curves represent the true relations between pressure and quartz-gage readings over the entire range, and can be used to read pressures for any gas whose viscosity and molecular weight are known, from the lowest detectable pressure up to the point where the slope becomes too steep for accurate reading. This extends the useful range from about 0.1 on the axis of ordinates (the limit of the lower range) to about 1 on the same axis, thus carrying us well into the range of the McLeod gage.

An approximate explanation of this relationship can be evolved as follows. An ideal gas, with infinite molecular free path, would presumably follow the asymptote over the entire range of pressures. Actual gases will begin to deviate from the asymptote at pressures at which their free paths become smaller than some definite value. Taking $L=3\eta/\rho\omega$, where L is the mean free path, ρ , the density of the gas $=\frac{Mp}{RT}$, and ω , mean molecular velocity $=\sqrt{\frac{8RT}{\pi M}}$, we have $L=\sqrt{\frac{\pi RT}{8}}\times\frac{\eta}{p\sqrt{M}}$.

It follows that different gases will begin to deviate from the asymptote at the same values of $p\sqrt{M}/\eta$. We may also suppose that at still higher

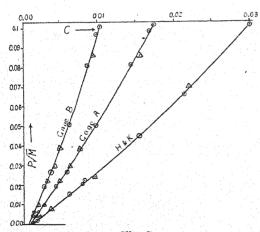


Fig. 3

pressures, different gases will deviate by the same amount when their mean free paths and, therefore, the values of $p\sqrt{M}/\eta$, are equal, so that their curves will remain coincident when $p\sqrt{M}/\eta$ is plotted against C/η . The presence of exponents different from unity is not explained.

Although the gages here described were constructed primarily for use in the upper range, they can also be used in the lower range, but

are not quite so sensitive as those of Haber and Kerschbaum. Fig. 3 shows the curves for air and hydrogen in Cartesian coördinates, together with one of Haber and Kerschbaum's. The freedom from harmonic vibrations secured by bifilar construction is particularly valuable here, as undesired modes of vibration, once set up, persist for a long time; the gage cannot be

read until they have died out. It will be noticed that the relation between C and $\rho\sqrt{M}$ is not strictly linear, even in this range.

The fact that the quartz-fiber manometer reads in terms of $p\sqrt{M}$ rather than p alone of course limits its applicability to those cases in which the gas to be measured has a known molecular weight, or is a mixture in known proportions of gases of known molecular weights. On the other hand, if M is unknown it can be determined by comparing the quartz-gage readings with those of some other form of delicate manometer, such as Carver's, which reads p directly. Evidently, this would furnish a method for identifying an unknown gas, analyzing a mixture of known gases of different molecular weights, and investigating the possibility of dissociation, at very low pressures. The method could be extended to higher pressures, in the first two cases, by reversing the principle of the McLeod gage; that is, by expanding the unknown gas in a sufficiently large ratio to bring it within the optimum range of the quartz-fiber gage.

Summary

A form of bifilar quartz-fiber manometer is described, from which troublesome harmonic vibrations are eliminated.

A method is described by which the instrument may be read up to pressures of 0.1 to 1 mm., depending on the gas used. The method involves calibration over the whole range with a permanent gas and a McLeod gage and, in addition, either a single measurement with the gas used and a McLeod gage at relatively high pressure, or a knowledge of the viscosity of the gas. So extended, the range of the instrument overlaps that of the McLeod gage, even with easily condensable vapors.

It is suggested that the gage may be used to determine molecular weights of gases at very low pressures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

ERRORS IN THE DETERMINATION OF HYDROGEN SULFIDE

By Fred H. Heath and Frank A. Lee Received April 11, 1923

Considerable interest is attached to a knowledge of the quantity of hydrogen sulfide present in natural waters. Such data are of value to the chemist, biologist and the public health officer. Hydrogen sulfide in natural waters is thought to be derived from both organic and inorganic sources and the quantity of it present in any water is likely to undergo rapid and rather great changes. Hydrogen sulfide in solution is rapidly oxidized and careful tests on solutions of the gas in distilled water show that 50% of the hydrogen sulfide may be lost in this way while a solution is kept overnight in a closed container at room temperature. Con-

sequently, the necessity for working with freshly obtained samples of natural waters is evident.

The investigations summarized in this article are the result of experimental work carried on for two summers at the North Dakota Biological Station at Devil's Lake, N. D. Further experiments were conducted at the University of Washington.

Natural waters of the lake region of North Dakota are typical saline waters of such a kind as will cause serious errors in the iodimetric determination of hydrogen sulfide. These lake waters are quite saline and are rich in alkali sulfates and carbonates. They contain considerable magnesium bicarbonate and some calcium bicarbonate. Total solids vary from 12000 to 25000 parts per million. In some instances the sulfate content of the water was more than half of the content of total solids. There appeared to be a slow bacterial reduction of sulfate to sulfide which caused a gradual precipitation of iron as iron sulfide. In many instances samples of mud from the lake bottom evolved considerable hydrogen sulfide upon treatment with hydrochloric acid. Analyses of such mud frequently showed a content of 10% to 12% of iron.

Waters of this lake region contain moderate amounts of ammonia and nitrates. Nitrites are generally absent during summer months.

Methods Now Used for Determination of Hydrogen Sulfide in Water.—In one colorimetric method¹ a lead salt precipitates brown lead sulfide or gives a brown color, the depth of which is dependent upon the amount of sulfide present. The color thus obtained is matched against that of lead sulfide derived from a known quantity of lead salt, and in this way the amount of hydrogen sulfide is measured. Waters rich in chlorides, sulfates or carbonates are not well adapted to the use of this method, since the chloride, sulfate and carbonate of lead are insoluble salts and would precipitate.

The iodimetric method for the determination of hydrogen sulfide is based upon the chemical changes which are illustrated by the following equations: $H_2S + I_2 = 2HI + S$; and $I_2 + 2 \text{ Na}_2S_2O_3 = \text{Na}_2S_4O_6 + 2 \text{ NaI}$.

To a measured quantity of the water is added a known excess of a standard solution of iodine. After a short time the excess of iodine is determined by titration with a standard solution of sodium thiosulfate. The hydriodic acid remains in the solution, and at the high dilution existing the free sulfur is in the colloidal form and does not precipitate. The iodine used is taken as a measure of the amount of hydrogen sulfide present. This process assumes that there is no substance present, other than hydrogen sulfide, which is capable of reacting with iodine. Such a condition does not exist except in very pure waters.

Effect of Organic Matter

Organic matter in general, either animal or vegetable, reacts with iodine and would therefore have a tendency to show a content of hydrogen sulfide somewhat greater than the true value.

Effect of Alkalinity

It is well known that the halogens react readily with hydroxides and carbonates. In iodimetry the presence of alkaline hydroxides or carbon¹ Winkler, Z. anal. Chem., 52, 641 (1913).

ates must be avoided, because of the reaction between these substances and iodine. Bicarbonates do no harm since they do not react with iodine.

In natural waters we often find carbonate and bicarbonate alkalinity. The former would cause absorption of iodine and consequently the amount of hydrogen sulfide as determined would be higher than the true value. The magnitude of this effect as tested upon natural waters of an average alkalinity is shown in Table I. The alkalinity of the water sample was determined by titration of a separate sample of water.

TABLE I

EFFECT OF CARBONATE ALKALINITY OF WATERS ON IODIMETRIC DETERMINATION OF HYDROGEN SULFIDE

Parts per million of hydrogen	sulfide	as :	measu	ired by	iodine	absorbed		
Before neutralization	2.0	3.	5	4.9	6.1	6.7	7.3	5
After neutralization	none	0.	2	0.06	0.2	none	0.6	റ

These samples were from different sources and their alkalinity varied somewhat, but each sample was carefully neutralized before making the tests recorded in the second line. The errors due to carbonate alkalinity are evident.

Effect of Nitrates

In order to test the effect of nitrates a solution of hydrogen sulfide was prepared in purified distilled water, and the concentration determined by the iodimetric method, using $0.01\ N$ solutions of iodine and sodium thiosulfate. To guard against changes in concentration of the hydrogen sulfide solution, because of oxidation, all tests were made immediately after the standardization of the solution. Measured portions of a dilute standard solution of potassium nitrate were then added to known volumes of the solution of hydrogen sulfide, followed by an iodimetric determination of the latter substance in the usual way. Results are given in Table II.

Table II

Effect of Nitrate upon the Iodimetric Determination of Hydrogen Sulfide

Quantity of nitrogen added as KNO ₃ G.	Volume of the solution Cc.		million of en sulfide Found by titration	Quantity of nitrogen added as KNO ₂ G.	Volume of the solution Cc.		er million of en sulfide Found by titration
0.004	150	76.0	71.0	0.004	200	5.87	3.0
.004	150	76.0	70.7	.008	200	5.87	1.9
.012	150	76.0	67.0	.002	200	0.70	0.56
.004	200	5.87	2.8	.006	200	0.70	0.50

From these results it is evident that the presence of nitrates causes the titration process to give values for hydrogen sulfide which are distinctly too low. Similar tests show that sodium nitrate acts like potassium nitrate. The explanation of this effect must be either that there is a loss of hydrogen sulfide or that iodine is liberated by chemical reaction in the course of the determination. It was found that nitrate in concentrations similar to those which occur in natural waters, does not oxidize the hydriodic acid formed, at least within any reasonable time, and further search for the cause of the low results was fruitless.

Effect of Nitrites

In order to test the action of nitrites a procedure was followed similar to that used in testing the effect of nitrates. A solution of hydrogen sulfide in pure water was prepared and standardized by the iodimetric method. To portions of this solution of the gas were added known quantities of freshly prepared standard solutions of nitrite, after which the iodimetric procedure was followed as usual. Results of such tests are given in Table III.

TABLE III

	-									
77			- NT-was market			Y	DETERMINATION		**	~
15.10	RECT	α	NITTITLE	HPON	THE	LODIMETRIC	1 1277 E D MITNE A TITO NE	OT	I TANDOUGHT	WALK STABLES
		V# .	w. i watterward	01 011	~~~~	TODAMATICIC	TO THE TAXABLE TAXABLE TO TA	Or	TTTDWOGTM	COMPADE

Quantity of nitrogen added as sodium nitrite G.	Volume of the solution Cc.		er million of yen sulfide Found by titration	Quantity of nitrogen added as potassium nitrite G.	Volume of the solution Cc.		million of en sulfide Found by titration
0.003	250	9.84	10.12	0.004	120	76.00	87.3
.004	250	9.44	10.00	.004	120	76.00	85.6
.012	250	9.24	10.00	.004	120	76.00	90.7
.021	250	8.64	9.92	.008	120	76.00	88.5
.030	250	8.04	9.92	.004	200	5.87	8.9
.018	250	6.40	7.20	.004	200	5.87	9.2
.024	250	6.40	7.40	.008	200	5.87	11.5
.030	250	6.20	7.68			1	

The presence of nitrites evidently causes high results in the iodimetric determination of hydrogen sulfide. In other words there is less free iodine in the solution to be titrated by sodium thiosulfate than should be there for the content of hydrogen sulfide known to be present. In order to interpret these results it will be necessary to account for some chemical changes which use up excess of iodine, due perhaps to a product formed by the action of hydrogen sulfide on a nitrite.

The chemical changes shown by the following equations appear as possibilities in connection with the explanation of the results of experiment.

Equation 1 shows liberation of iodine and this does occur in concd. solutions of iodide and nitrite upon acidification. It represents the determination of iodides in presence of other halides. However, this action is contrary to the fact that small amounts of nitrite in very dilute solutions cause too high results in the determination of hydrogen sulfide.

Equation 2 expresses the oxidation of nitrite to nitrate by iodine in dilute solution. Colorimetric tests for nitrate mixed with small amounts of iodine and nitrite in very dilute solutions do not seem to show any appreciable formation of nitrate.

Equation 3 calls for the formation of the compound nitrosyl iodide, NOI. Since nitrosyl bromide is a very unstable substance, even at low temperatures, it is very unlikely that nitrosyl iodide could be formed.

The chemical process illustrated by Equation 4 has been patented² for use in connection with the Le Blanc soda process. That this is the reaction which probably takes place has been shown by passing hydrogen sulfide into a very dilute solution of sodium nitrite, acidifying with sulfuric acid, boiling off the hydrogen sulfide and testing for ammonia by the Nessler method. Positive results were obtained. All of the solutions and reagents used were tested, and found to be ammonia free. Both sodium and ammonium hydroxides will use up iodine. Ammonium hydroxide and iodine may also form nitrogen iodide.

Effect of Soluble Iodide

It was thought best to attempt the iodimetric determination of hydrogen sulfide in the absence of any alkali metal iodide, so as to eliminate any possible interference by potassium iodide. For this purpose a standard dilute solution of iodine dissolved in water was titrated; the endpoint was less distinct than usual, due to the absence of iodide. As in the previous instances, it was found that nitrites cause high results, while nitrates cause low results.

In further tests it was found that sodium chloride, calcium chloride, magnesium chloride and urea had no effect upon the accuracy of the determination.

Summary

In view of the very evident errors caused by the presence of small quantities of salts the authors recommend that use of the iodimetric process for the determination of hydrogen sulfide in natural water be discontinued. In order to eliminate errors due to the action of nitrites, nitrates and alkali salts we suggest that natural waters be tested for hydrogen sulfide by the colorimetric method of W. Mecklenburg and F. Rosenkränzer in which methylene blue is formed.³ The need of a qualitative as well as a quantitative method is further shown by the fact that some of the samples from Devil's Lake gave no test by this latter method, but positive results were obtained by the iodimetric method.

SEATTLE, WASHINGTON

² Görlich and Wichmann, Ger. pat., 87,135; Ber., 39, 606 (1896).

³ Mecklenburg and Rosenkränzer, through C. A., 8, 1938 (1914).

[Contribution from the Insecticide and Fungicide Laboratory, Miscellaneous Division, Bureau of Chemistry, United States Department of Agriculture]

EMULSIONS OF MINERAL OIL WITH SOAP AND WATER: THE INTERFACIAL FILM

By EDWARD L. GRIFFIN

Received April 14, 1923

Emulsions in which mineral oil is dispersed in water by means of soap are largely used as insecticides. Both kerosene and higher fractions of petroleum are used. Certain difficulties in the manufacture and use of these emulsions make important an understanding of the actual state of the constituents in an emulsion.

Much work on emulsions of this type has already been done, but the exact manner in which the soap functions is still in dispute. Several theories have been advanced to explain its action, the most important being as follows.

- 1. Emulsification depends principally upon obtaining the proper surface tension and viscosity. 1,2,3
- 2. Emulsions consist of droplets of oil surrounded by a film of discrete, insoluble particles which are more easily moistened by water than by oil.⁴
- 3. Emulsions are made by the dispersion of oil, not in a water solution of soap or other emulsifier, but rather in a hydrated colloid. Enough of the colloid must be present to bind all the water.⁵
- 4. Emulsions consist of droplets of oil which are surrounded by more or less plastic films, 6,7,8,9
- 5. Emulsions consist of droplets of oil in water, with an interface composed of molecules of a third substance, the molecules being so orientated that the group which has an affinity for water is dissolved in the water, while that which has an affinity for the oil is dissolved in the oil.^{10,11}

Very little work had been done to prove this last theory. In fact Harkins, Davies and Clark said that "what is presented in this paper on the problem of the formation of colloids and emulsions is only preliminary in nature but much may be expected from the application of the principles in regard to the setting of molecules in surfaces to this problem."

- ¹ Quincke, Ann., 35, 571 (1888).
- ² Donnan, Z. physik. Chem., 31, 42 (1899).
- ³ Donnan and Potts, Kolloid-Z., 7, 208 (1910).
- 4 Pickering, ibid., 7, 11 (1910).
- ⁵ Fischer and Hooker, "Fats and Fatty Degeneration," John Wiley and Sons, 1917.
- ⁸ Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921.
- ⁷ Briggs, J. Phys. Chem., 19, 210 (1915).
- 8 Holmes and Cameron, This Journal, 44, 66 (1922).
- ⁹ Clark and Mann, J. Biol. Chem., 52, 157 (1922).
- 10 Langmuir, This Journal, 39, 1848 (1917).
- 11 Harkins, Davies and Clark, ibid., 39, 541 (1917).

Theoretical Consideration

If a kerosene emulsion consists of droplets of kerosene, each surrounded by a film of soap 1 molecule thick, the whole surrounded by a soap solution containing the unabsorbed soap, it might seem possible to determine the soap extracted from the water solution in the formation of the emulsion.¹² The quantity of soap removed from aqueous solution would be directly proportional to the area of interface formed and entirely independent of the concentration of soap originally present, provided, of course, that sufficient soap is present to form the film.

It is also possible to measure the area of the droplets formed. From a comparison of the amount of soap removed by each cubic centimeter of kerosene with the area of interface formed by the same amount, the average area covered by each molecule of soap can be calculated.

In a molecule the size of that of stearic or oleic acid the replacement of a hydrogen atom by sodium would hardly be expected to greatly increase the average area occupied by a molecule and in this case the results would be expected to agree rather closely with those obtained by Langmuir for the average area occupied by each molecule of the various fatty acids when placed on water in a film 1 molecule thick (46, 22, and 21×10^{-18} sq. cm. for oleic, stearic, and palmitic acids, respectively). The possibility that the soap might be heavily hydrated is not precluded. In this case the area occupied by each molecule of soap might be much greater than that occupied by a molecule of the corresponding fatty acid.

When kerosene is emulsified in fairly dilute sodium oleate solution by shaking and then allowed to stand, the oil droplets cream out at the top, leaving a clear or nearly clear aqueous soap solution at the bottom. If this soap solution is analyzed before and after emulsification of the kerosene, the difference in the quantity of soap carried will be that taken up by the kerosene.

The area of interface may be calculated as follows. An oil emulsion contains droplets of various sizes. Let us assume that these droplets are assigned to various classes whose radii, expressed in centimeters, are r_1 , r_2 , r_3 , r_4 , respectively. Let us measure a large number of drops, denoting those with radius r_1 by x_1 , those with radius r_2 by x_2 , those with radius r_3 by x_3 , and so on. The area of interface associated with each cubic centimeter of kerosene is the sum of the areas of these droplets divided by the sum of their volumes or

$$\frac{3(x_1r_1^2 + x_2r_2^2 + x_3r_3^2 + \dots)}{x_1r_1^3 + x_2r_2^3 + x_3r_3^3 + \dots}$$

¹² Briggs, Ref. 7, made titrations which showed that soap was removed but says that absolute measurements were not obtained. His results are to be considered only as comparative.

The area of interface associated with 1 cc. of kerosene, divided by the number of molecules of soap removed, gives the area of interface formed for each molecule of soap removed. Millikan's value, 13 for the number of molecules in a mole (6.06 \times 10 23) was used.

Experimental Part

Materials Used

U. S. P. stearic and oleic acids were used. The stearic acid had been purified by alcohol. While both of these acids usually contain small amounts of impurities, the errors in the other measurements are such that it was believed that the results would not be affected.

A sample of impure commercial palmitic acid, having a yellow color, and somewhat soft, was first employed. Later, a sample of pure palmitic acid with a melting point of 62° and an iodine number zero, was obtained from Dr. George E. Jamieson of the Bureau of Chemistry.

Emulsions

Soap solutions were made as follows. The calculated amount of fatty acids was weighed into a flask. About 500 cc. of water was added, and heat was applied when necessary to melt the acid; the mixture was then shaken while the calculated amount of normal alkali necessary to form a neutral soap was added, the mixture heated and shaken until all dissolved. This was then cooled to room temperature, made up to 1 liter, and mixed by shaking. An approximately 0.2 or 0.1 M solution was usually prepared as a stock solution, weaker solutions being made from it by dilution as needed.

Except where otherwise stated, emulsions were made by the following procedure. The required volume (usually 100 cc.) of soap solution was measured into a flask and an equal volume of kerosene was added. Then the whole mixture was drawn up into a large pipet by vacuum and rapidly expelled by compressed air, repeating the process about 10 times. The emulsified product was next poured into a cylinder and the cylinder was stoppered and allowed to stand. One or two days later when the emulsion had come to equilibrium, the contents of the cylinder were run from end to end several times to guard against local differences of concentration, then allowed to stand, usually for about 2 weeks, until the oil drops had arisen to the top as a cream, leaving a clear or nearly clear aqueous lower layer sufficient for analysis.

Another portion of the same soap solution was preserved under the same conditions for comparative analysis.

Fatty Acid Determination.—Twenty-five or 50 cc. of the solution to be analyzed was pipetted into a 120cc. Squibb funnel. Enough N sulfuric

¹³ Millikan, Phil. Mag., [6] 34, 1 (1917).

acid was then added to break down the soap and leave a slight excess of acidity, followed by 40 cc. of u. s. p. ether. The contents of the funnel were well shaken and allowed to separate into layers, and the lower layer was drawn into Funnel 2. About 40 cc. of ether was added to this and the material was well shaken and allowed to separate. The lower layer was drawn into Funnel 3, where it was again washed with ether and then discarded. The ether layers in the 3 funnels were next washed with water, until the last washing contained no more than traces of acid, after which they were combined in a beaker. Nearly all of the ether was evaporated on the steam-bath. About 50 cc. of neutral alcohol was poured into the beaker containing the fatty acids and the acids were titrated with $0.1\,N$ sodium or potassium hydroxide solution, using phenolphthalein as an indicator.

Analyses were made of the clear layer from the emulsion and of the soap solution from which the emulsion was made. The quantity of fatty acid found was calculated to moles per liter. The difference between the moles of acid found per liter in the original solution and that found in the lower layer from the emulsion represents the number of moles removed by each liter of the kerosene inasmuch as the kerosene and the soap solution were used in equal volumes. The value thus obtained, divided by 1,000, gives the number of moles removed by 1 cc. of kerosene.

Measuring the Droplets.—The contents of the cylinder containing the emulsion were carefully run from end to end several times in order to mix it without changing the size of the droplets. A small quantity of the emulsion was then poured into distilled water in an Erlenmeyer flask and the flask was rotated until an even mixture was obtained. A small quantity of this diluted emulsion was placed on a microscope cover glass by means of a platinum loop, and mounted on a ground-glass slide just as a hanging drop of bacterial culture is mounted to study the motility of an organism. The droplets were immediately examined under the microscope, using a 4 mm. objective and a No. 10 evepiece containing a micrometer disc. The slide was set at random and the sizes of all the droplets whose centers appeared on the scale were recorded to the nearest half scale-division up to 3, above that to the nearest division. Each scale division was equal to 0.00038 cm. The tube was moved up and down so as to find all the droplets in the area. The slide was moved from place to place until about 200 droplets had been measured and the number in each class obtained.

Sodium and Oleic Acid Removed by Emulsification

Emulsions were made from sodium oleate solutions of various concentrations and kerosene. When a soap solution containing 0.002 mole or less of sodium oleate per liter was used, the emulsion formed was not permanent. Permanent emulsions were formed with soap concentrations

ranging from 0.003 to 0.124 mole per liter. Oleic acid was removed from the aqueous layer in the process of emulsification, the loss varying from 0.0022 to 0.0086 mole per liter. The area of interface formed was from 3,700 to 11,400 sq. cm. for each cubic centimeter of kerosene. The area of interface formed for each molecule of oleic acid lost was from 21 \times 10⁻¹⁶ to 39 \times 10⁻¹⁶ sq. cm.

These values, although somewhat lower, are of the same order of magnitude as those obtained by Langmuir for the average area of 1 molecule of oleic acid in a surface film (46×10^{-16} sq. cm.). If they differed from those for surface films it was expected that they would be higher for the reason that the sodium atom is larger than the hydrogen atom and also because hydration of the soap may be expected. It was considered possible that part of the oleic acid removed had gone into solution in the kerosene and not into the interface. If this were the case, more oleic acid than sodium would be extracted from the soap solution in making an emulsion and an excess of sodium would remain in the aqueous layer. It was decided, therefore, to conduct experiments in which both the sodium and the oleic acid removed by emulsification were determined.

Sodium Determination.—Sodium was determined as follows. A 25-or 50cc. aliquot portion of the solution was evaporated to dryness in a platinum dish and ignited at a low temperature. An excess of N sulfuric acid was added and the whole was evaporated to dryness and ashed completely. The silica was dehydrated by evaporation with hydrochloric acid, and drying for 1 hour at 110° . It was then treated with hydrochloric acid, filtered, and washed, and the filtrate was evaporated to dryness in a weighed platinum dish. Water, 0.5 cc. of N sulfuric acid, and ammonia in excess were added, and this mixture was evaporated to dryness, ignited, and weighed as sodium sulfate. The results obtained are shown in Table I.

Table I

Sodium and Oleic Acid Removed from Solution on Emulsification

Concn. of sodium oleate in soap soin. Moles per liter	Materia from ac Sodium Moles pe	Oleic acid	Area of interface × 10 ⁻³ per cc. of kerosene Sq. cm.	of molec interfac	ction area ules in the e × 10 ¹⁶ Calc. from oleic acid
0.05	0.0038	0.0046	11.0	48	39
.025	.0037	.0049	10.3	46	35
.0125	.0037	.0058	10.9	49	31

In every case the loss of oleic acid exceeded the loss of sodium. Assuming that all of the sodium that disappeared from solution went into the interface in the form of a unimolecular layer of sodium oleate and that the excess oleic acid that disappeared went into solution in the kerosene, the areas calculated for the average cross section of a molecule of sodium oleate in the film agree very well with those obtained by Langmuir for a molecule of oleic acid in a surface film.

It was thought that reduction of the hydrolysis of the soap by the addition of sodium hydroxide might make the concentration of the undissociated fatty acid in the soap solution so small that the quantity taken into solution by the kerosene would be negligible. An emulsion containing 0.1 mole of sodium oleate and 0.01 mole of sodium hydroxide per liter was therefore made. Equivalent quantities of sodium and oleic acid (0.0028 mole per liter) were removed from the solution. The interfacial area formed per cubic centimeter of kerosene was 7.45×10^3 sq. cm. and the area for each molecule of sodium oleate removed from the solution was 44×10^{-16} sq. cm.

The fact that the quantities of sodium and oleic acid absorbed were equivalent agrees with, but does not prove our theory. Since certain fatty acids form acid salts with the alkali metals, it was considered possible, in the case of the neutral sodium oleate emulsions with kerosene, that an acid salt might go into the interface, as suggested by Pickering. This would account for the discrepancy in the quantities of sodium and of oleic acid absorbed. A direct method of extracting sodium oleate solution with kerosene was therefore sought.

No method presented itself of breaking an emulsion after it had been formed, without changing conditions in the mixture to such an extent that the results would be valueless. An extraction was, therefore, made in a rotating machine in the following manner, care being taken that no emulsion was formed. One hundred cc. of the soap solution was pipetted into a 300cc. round bottle; the formation of bubbles was carefully avoided. One hundred cc. of kerosene was carefully placed on top of the soap solution by means of a pipet, and in such a way that a smooth surface between the kerosene and the soap solution was maintained. The bottle was stoppered and carefully fastened on the rotating machine so that its long axis was parallel to the axis of rotation. The machine used had a diameter of rotation of about 15 inches and made 30 revolutions per minute; when it was properly run no emulsion resulted. After the required period of rotation the bottle was removed, and an aliquot portion of the clear kerosene was taken. An equal volume of neutral alcohol was added to the kerosene and the mixture was titrated with 0.1 N alkali, using phenolphthalein as an indicator. The mixture was shaken after each addition of alkali. A value of 0.10 cc. of 0.1 N alkali for 50 cc. of kerosene was subtracted in all cases as representing the value of a blank experiment.

To determine the time necessary to run the machine to insure complete extraction, 4 bottles, each containing sodium oleate solution of the same strength and kerosene, were placed on the machine which was set in motion. One bottle was removed at the end of each successive half-hour period up to 2 hours; the solutions then required 0.60, 0.65, 0.60 and 0.65 cc. of $0.1\,N$

¹⁴ Pickering, J. Chem. Soc., 91, 2001 (1907).

sodium hydroxide, respectively; that is, at the end of a half hour the maximum amount of acid had been extracted by the kerosene. In the extractions noted in this paper 1 hour was the time ordinarily used, thus securing a sufficient margin of safety.

A portion of kerosene which had been used to extract sodium oleate solution by the method described and another portion obtained by breaking down an emulsion with heat were ignited. No weighable amount of ash remained, indicating that sodium oleate as such is not dissolved by kerosene.

Experiments were conducted to determine the quantity of sodium and oleic acid removed from the solution on emulsification and also that which was dissolved in the kerosene. The difference between the quantity of oleic acid dissolved in the kerosene and the total acid removed on emulsification was the part which went into the interface. The experimental results are shown in Table II.

Table II

Experimental Data on Emulsions of Kerosene with Sodium Oleate Solution

Conen. in solution Sodium oleate Mcles per l	of Sodium hydroxide	Materia inter Sodium G. atoms or m	face Oleic acid	Area of interface × 10 ⁻³ per cc. of kerosene Sq. cm.	Av. cross area of sodi molecule Calc. from sodium Sq. cm.	ium oleate	
0.100	0.01	0.0028	0.0028	7.45	44	44	
.100		.0031	.0028	8.47	45	50	
.020		.0024	.0023	7.17	49	51	
.005		.0024	.0023	6.87	47	49	
.02	0.002	.0026	.0026	7.9	50	50	
.005	.0005	.0026	.0024	7.40	47	51	
.0125		.0007	.0007	2.00	47	47	
.01		.0009	.0009	2.40	44	44	
.0033	.01		.0025	7.92		52	
.01°	• • •		.0032	9.73		50	
	 ** ** ** ** ** ** ** ** ** ** ** ** **						

^a This emulsion was made and kept at 55°.

Emulsions with Stearic Acid Soap

Sodium stearate is so insoluble in water that it is impossible to study emulsions made from it and kerosene by the method used for the sodium oleate emulsions. After a $0.05\,M$ solution of potassium stearate made by the method described had stood at room temperature, soap separated. All of the experiments, therefore, were run at a higher temperature, 55° being chosen, but the final dilution for measuring the droplets was made at room temperature. If there is a unimolecular layer of soap around the oil droplets, the cross-sectional area, since it is measured at room temperature, will not be changed by the higher temperature of creaming out.

Under these conditions large quantities of glass were dissolved, as shown by the silica in the ash from the soap solution and by the etching of the cylinders. The potash determinations, therefore, were unreliable and were not used.

The stearic acid in the interface was determined by the methods used for oleic acid in the emulsions from sodium oleate. The kerosene was extracted at about 55°. The results thus obtained are shown in Table III.

TABLE III

EXPERIMENTAL DATA ON EMULSIONS OF KEROSENE WITH POTASSIUM STEARATE
SOLUTION

Conen, in soap solution of potassium stearate Mole p	Potassium hydroxide er liter	Stearic acid in the inter- face Mole per liter	Area of interface X 10 ⁻³ per cc. of kerosene Sq. cm.	Cross section area of mol- ecules in interface × 1015 Sq. cm.
0.025	• •	0.0050	7.48	25
.0062		.0045	6.91	25
.0031	• •	Er	nulsion broke	
.100	0.01	.0043	7.60	29
.020	.01	.0033	6.21	31
.005	• •	.0038	5.64	24
				Av. 27

Emulsions with Palmitic Acid Soap

Emulsions made from a commercial sample of palmitic acid in the manner already described were held at a temperature of 40° while they settled. The cross-sectional area of the molecules in the interface determined in these experiments varied from 32×10^{-16} to 44×10^{-16} sq. cm.

These results did not check well with the cross-sectional areas obtained for palmitic acid by Langmuir (21×10^{-16} sq. cm.). In fact, they agreed better with the values for unsaturated fatty acids. The iodine number of the palmitic acid was very high, indicating the presence of a large amount of unsaturated acids. These results, therefore, cannot be considered of any value in determining the cross-sectional area of molecules of palmitic acid in an interface.

Accordingly, a sample of c. P. palmitic acid having an iodine number of zero was obtained from the Oil, Fat and Wax Laboratory of the United States Bureau of Chemistry. The results obtained by using this acid at 55° are shown in Table IV.

Table IV

Experimental Data on Emulsions of Kerosene with Potassium Palmitate

Expts.	Concn. in soap solution of Potassium Potassium palmitate hydroxide Mole per liter	Palmitic acid in the interface Mole per liter		Cross section area of mole- cules in inter- face × 1016 Sq. cm.
37	0.01	0.0036	7.1	32
38	.01	.0047	7.6	27
39	.01 0.01	.0040	7.6	31

Av. 30

Conclusions

The experiments here reported show that when kerosene is emulsified with a neutral soap solution the soap is partially hydrolyzed and some of the fatty acid is dissolved in the kerosene. This hydrolysis may be prevented, or at least reduced to a negligible amount, by the addition of free alkali. No sodium or potassium is dissolved in the kerosene.

In the formation of an emulsion a certain quantity of soap is removed from the soap solution and does not go into the kerosene. It must, therefore, go into the interface between the kerosene and the remaining soap solution. The quantity of soap absorbed is (within the experimental error) proportional to the area of interface formed and is not dependent upon the concentration of soap originally in the solution.

The droplets of oil in a good emulsion must be small. This work shows that when a quantity of soap insufficient to form the interface for these droplets is present, the resulting emulsion is not stable. All of the emulsions made with very small amounts of soap "broke" on standing.

On the theory that these considerations indicated that the interface consists of a monomolecular layer of soap, the area of interface formed by each molecule of soap present (or the average cross-section of the soap molecules) was calculated. The results bore out the theoretical belief that the areas thus measured should be the same as, or somewhat greater than, those measured by Langmuir for the corresponding fatty acids in surface films. The average values for the soaps as determined by this method are 48, 27 and 30 \times 10^{-16} for sodium oleate, potassium stearate and potassium palmitate, respectively, and those for the corresponding fatty acids as determined by Langmuir are 46, 22 and 21×10^{-16} , respectively.

These results agree with the values expected and show that the film formed at the interface must be 1 molecule thick. The only other possible explanation would be the formation of a film of heavily hydrated soap of constant thickness at the interface. As these films came from solutions of widely varying concentration and as the hydration of soap in precipitates depends on the concentration of the solution from which it is precipitated, the second theory becomes untenable.

It may, therefore, be concluded that a unimolecular film must be formed at the interface when kerosene is emulsified with solutions of soap.

Summary

- 1. In an emulsion of mineral oil with soap and water, part of the soap is hydrolyzed, the fatty acids being dissolved by the oil droplets and the alkali remaining in aqueous solution.
- 2. Fatty acids may be kept from dissolving in the oil by the addition of excess alkali.
 - 3. Part of the soap forms unimolecular films around the oil droplets.

The average areas occupied by each molecule of sodium oleate, potassium stearate and potassium palmitate, were found to be 48, 27 and 30 x 10^{-16} sq. cm., respectively. These areas agree rather closely with those found for the corresponding fatty acids in unimolecular films on the surface of water.

- 4. In case there is insufficient soap to form a unimolecular film the emulsion is not stable.
 - 5. The excess soap remains in water solution.

WASHINGTON, D. C.

[Contribution from the Color Laboratory, Bureau of Chemistry, United States Department of Agriculture, No. 74]

ADSORBED MOISTURE AND WATER OF CRYSTALLIZATION IN CERTAIN COMMON DYES

By H. Wales and O. A. Nelson Received April 24, 1923

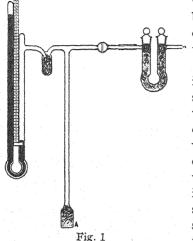
A discrepancy between the observed and calculated results for different samples of pure methylene blue when the molecular weight as given in the United States Pharmacopeia (C₁₆H₁₈N₃SCl.3H₂O) was used, always occurred during the work done on this dye in the Color Laboratory. As the authority for assuming the presence of 3 mols. of water of crystallization in this compound failed to give reliable experimental data, it was considered desirable to determine, if possible, whether or not the moisture in this dye, as well as in a few others, was present as adsorbed moisture or as water of crystallization.

From the literature, reference to which will be made as each dye is considered, it appears that no investigator has attempted to show by experiment how the moisture in his sample was held. The customary method was to heat the dye at a definite temperature for a definite period of time and calculate the amount of water present from the analytical determinations of elements. The water thus found was then considered in terms of mols. of water of crystallization when, from the data given, it might as readily be adsorbed water. Since adsorbed water is often held more tightly than the so-called water of hydration or crystallization, it seems obvious that the results obtained by such a method cannot be conclusive.

The primary object of this work was not so much to determine the quantity of water present in the dyes studied as to ascertain whether the water was present as adsorbed moisture or as water of crystallization.

Theoretically, if the vapor pressure of a hydrate be plotted against the weight of water present at constant temperature, the pressure remains constant until the last of the hydrate corresponding to this pressure has been removed. At this point the pressure drops to that of a lower hydrate,

if one is present, or to that of the anhydrous substance. Practically, however, these breaks are not always sharp. Beutell and Blaschke¹ found that in all cases where there was more than one hydrate, the dehydration on the surface of the particles proceeded further than in the interior, "where cohesion hindered the evolution of water vapor." The inside of the particles, therefore, consists of hydrates higher than those at the surface. This prevents a sharp transition from one hydrate to the next, and causes a rounding of the breaks in the curve which becomes more pronounced



with increase in the pressure difference between two hydrates. (Compare the curves for oxalic acid, crystal violet and tartrazin.)

If, however, the water in a compound is present as adsorbed water, the curve showing the relation of vapor pressure to water content will not have the breaks characteristic of the hydrate curves, but will be perfectly smooth and have a slope depending on the tenacity with which the water is being held. These two types are illustrated by the curves for hydrates, such as cupric sulfate pentahydrate or sodium carbonate decahydrate,² and by that of vapor pressure against water con-

tent curve of a substance containing adsorbed water.³ A vapor pressure-water content curve for oxalic acid (COOH)₂.2H₂O at 50° was determined to test the apparatus and also to obtain a curve for a known hydrate. The results are tabulated in Table I and shown diagrammatically in Fig. 2, Curve A.

Method.—Since the vapor pressure-water content curves of hydrates and substances containing adsorbed water are so distinctly different, the method used in determining which dyes are hydrates and which contained adsorbed water was that of determining the vapor pressure after removing a small increment of water, at constant temperature. The apparatus used was essentially the same as that described by Nelson and Hulett,⁴ a portion of which is shown diagrammatically in Fig. 1. About 1.5 g. of dye was weighed into Bulb A and a wad of fine glass wool was packed in, to prevent the dye from being carried over mechanically when the pressure in the system was lowered. The bulb was then sealed to the manometer

- ¹ Beutell and Blaschke, Centr. Minal. Geol., 1915, 199.
- ² Z. physik. Chem., 7, 241 (1891).
- ⁵ Hulett and Nelson, Trans. Am. Electrochem. Soc., 38, 103-119 (1920).
- 4 Nelson and Hulett, J. Ind. Eng. Chem., 12, 40 (1920).

as indicated in the illustration. The moisture was absorbed in phosphoric anhydride and the system was evacuated by means of a Toepler mercury

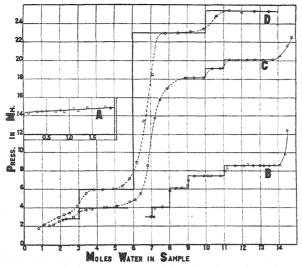


Fig. 2.—A, oxalic acid 2H₂O at 50°; B, crystal violet at 26° (subtract 5 mols.); C, tartrazin at 26°; D, tartrazin at 30°

pump. The pressure was read with the naked eye, directly from the manometer with an accuracy of about ± 0.2 mm.

			IAE	SLE I			
			Oxalic A	cid at 50°			
H ₂ O removed	H ₂ O to pure acid	H ₂ O in sample Mols.	Pressure Mm	H ₂ O removed	H ₂ O to pure acid %	H ₂ O in sample Mols.	Pressure Mm.
1.2	38.2	1.9	14.9	19.2	13.0	0.7	14.5
4.4	33.6	1.7	15.0	21.1	10.3	0.5	14.6
9.2	27.0	1.4	14.9	23.3	8.0	0.4	14.5
11.0	24.5	1.2	14.6	24.9	5.0	0.3	14.5
13.2	21.3	1.1	14.8	26.8	2.3	0.1	14.3
15.4	18.3	0.9	14.5	28.5	0.0	0.0	
17.2	15.7	0.8	14.6				

Methylene Blue (C₁₆H₁₈N₃SCl).—Previous work on the water content of methylene blue is very contradictory. Koch⁵ prepared 2 samples of methylene blue under identical conditions and found that one contained the equivalent of 4 molecules of water and the other the equivalent of 1.5 molecules. Both samples gave up the water completely at 110°. Bernthsen⁶ found that the salt dried in a desiccator lost an equivalent of 2 mols. of water at 100°, 2.5 at 130° and 3 at 150°. He claims to have heated to constant weight in each case. The American and French Pharmacopeias

⁵ Koch, Ber., 12, 592 (1879).

⁶ Bernthsen, Ann., 230, 139 (1885).

accept Bernthsen's figures and give the formula as $C_{16}H_{18}N_3SC1.3H_2O$. The German Pharmacopeia makes no mention of moisture in this compound.

Four samples of methylene blue made by different manufacturers were analyzed in the Color Laboratory and contained 11.44%, 11.58%, 12.42%

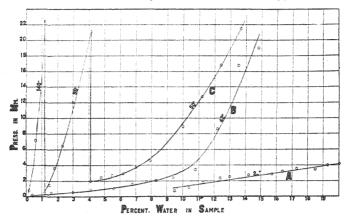


Fig. 3.—A, methylene blue at 28°; B, methylene blue at 42°; C, erythrosin at 50°, 90° and 140°

and 17.06% of water (calc. for 3 mols. of water: 14.46%). In every case the salts could be completely dehydrated by drying them at 110° for 1 day, thereby confirming Koch's results.

TABLE II
METHYLENE BLUE HYDROCHLORIDE

	28°			42°	
Water removed %	Water to pure color %	Pressure Mm.	Water removed %	Water to pure color	Pressure Mm.
0.0	20.6	7.5	4.9	14.8	19.0
0.5	20.1	4.2	5.6	13.5	16.8
1.0	19.3	4.0	6.8	12.2	8.7
1.7	18.5	3.5	8.2	10.8	3.5
2.8	17.3	3.6	9.4	9.4	2.5
3.5	16.4	3.2	10.3	8.3	2.1
4.1	15.7	2.9	11.5	6.8	1.6
5.3	14.2	2.8	12.5	5.6	1.1
6.3	13.0	2.6	13.7	4.1	0.9
6.9	12.4	2.4	14.6	3.0	0.6
7.8	11.3	1.8	15.8	1.6	0.3
8.5	10.4	1.2	16.8	0.4	0.2
9.2	9.5	0.8	17.1	0.0	0.0

The vapor pressure-water content curves of the sample containing 17.06% were determined at 28° and 42°, with the results shown in Table II and Fig. 3, Curves A and B. The curves show no indication of breaks,

thus indicating that the moisture in this dye is not present as water of crystallization. In the following tables the percentage of water has been recomputed to a pure color basis, for convenience in determining the degree of hydration.

The Zinc Chloride Salt of Methylene Blue.—The formula for the zinc chloride double salt of methylene blue is usually given as $(C_{16}H_{18}N_2SCl)_2$.— $ZnCl_2$. H_2O . Apparently the only authority for this is Bernthsen³ who found 2.13% of moisture (calculated for $1H_2O$: 2.27%). No mention was made of the temperature at which the moisture was evolved. Three samples of the zinc chloride salt of methylene blue analyzed in the Color Laboratory yielded 4.0%, 3.4% and 3.1% of moisture. Heating in an oven for 1 day at 110° was sufficient to remove all but very minute traces of water.

The vapor pressure-water content curve was determined on the sample containing 4.0% of water. The results again indicated the absence of water of hydration. It should be noted that the total percentage of water obtained by the authors' method agreed well with that obtained by heating in an over.

Table III

Methylene Blue Zinc Chloride at 40°

H₂O removed	H ₂ O to pure color %	Pressure Mm.	H ₂ O removed	H ₂ O to pure color	Pressure Mm.
0.0	4.2	24.0	2.0	2.1	2.9
0.3	3.9	18.4	2.4	1.65	1.0
0.6	3.5	13.5	2.8	1.2	0.8
1.2	2.9	8.0	3.2	0.8	0.3
1.5	2.6	6.0	3.4	0.6	0.2
1.7	2.3	3.4	4.0	0.0	• • •

Crystal Violet, C₂₃H₃₀N₃Cl.—Crystal violet or hexamethyl-p-rosaniline hydrochloride is stated to contain 8 molecules of water of crystallization.⁹ Green¹⁰ gives the same figure, and Schultz¹¹ gives 9 molecules.

A sample of commercial crystal violet was found on analysis to contain 4% or about 1 molecule of water. After recrystallization from water and drying for 24 hours at room temperature in a desiccator, this sample yielded 29.5% of water. The vapor pressure-water content curve for this sample (Fig. 2, Curve B), determined at 26° , showed breaks corresponding to hydrates containing 9, 6, 4, 3 and 2 molecules of water. The presence

⁷ By pure color basis is meant the parts of water per 100 parts of anhydrous dye. A dye containing 20% of water, therefore, would contain 25% on a pure color basis.

⁸ Bernthsen, Ann., 251, 81 (1889).

⁹ Kraft, Ber., 32, 1611 (1899).

¹⁰ Green, "Organic Coloring Matters," The Macmillan Co. N. Y., 1908.

¹¹ Schultz, "Farbstofftabellen," Weidmannsche Buchhandlung Berlin, 1914.

of lower hydrates was not determined, owing to appreciable sublimation of the dye at pressures below 3 mm. 12

TABLE	IV		
Chromat Triot	ET	ΑT	269

:	H ₂ O removed %	H ₂ O to pure color	H ₂ O in sample Mols.	Pressure Mm.	H ₂ O removed %	H ₂ O to pure color %	H ₂ O in sample Mols.	Pressure Mm.
	0.0	41.9	9.5	12.5	13.0	23.5	5.3	7.5
	0.3	41.4	9.4	9.9	13.5	22.8	5.1	7.5
	1.2	40.2	9.1	8.7	14.2	21.5	4.9	7.5
	2.1	38.8	8.8	8.7	15.8	19.4	4.4	7.5
	3.0	37.6	8.5	8.6	17.0	17.7	4.05	7.0
	4.1	36.1	8.2	8.6	17.1	17.6	4.0	6.5
	4.8	35.2	8.0	8.6	18.0	16.3	3.7	6.2
	5.6	33.9	7.6	8.6	19.1	14.8	3.35	6.1
	7.3	31.5	7.2	8.7	20.1	13.3	0.8	5.9
	7.4	31.4	7.1	8.6	21.3	11.6	$^{2.6}$	4.1
	9.1	29.0	6.6	8.6	22.4	10.1	$^{2.3}$	4.0
	10.4	27.1	6.2	8.4	23.0	9.3	2.1	3.0
	10.5	26.9	6.1	8.0	23.4	8.6	1.95	3.0
	11.4	25.5	5.8	7.5				

Magenta.—Both rosaniline and p-rosaniline-hydrochlorides are stated to contain 4 molecules of water of crystallization. 9,10,111 As neither of

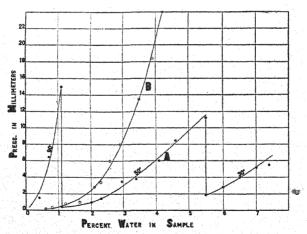


Fig. 4.—A, magenta at 30°, 50° and 90°; B, methylene blue ZnCl₂ at 40°

these compounds was available, carefully purified magenta, which is an approximately equimolecular mixture of the two, was examined. Table V and Fig. 4, Curve A, show the results obtained on this sample. The vapor

¹² Green and Schultz (Ref. 10; Ref. 11) also record the anhydrous dye as existing in cantharides-green, glistening crystals and the hydrated form as bronzy crystals. This is perhaps due to the state of subdivision, as there was no noticeable change in color on dehydration in the sample used.

pressure-water content curve of this mixture is perfectly smooth, with no indication of a break.

TABLE V MAGENTA

H ₂ O removed %	H ₂ O to pure color	Pressure Mm.	Temper- ature °C.	H ₂ O removed %	H ₂ O to pure color %	Pressure Mm.	Temper- ature ° C.
0.0	7.4	5.5	30	4.5	2.95	3.6	50
0.7	7.0	5.2	30	5.1	2.3	1.5	50
1.2	6.5	4.0	30	5.3	2.0	1.0	50
1.6	6.0	2.8	30	6.2	1.1	0.2	50
2.1	5.5	1.9	30			15.0	90
		11.2	50	6.5	0.7	6.5	90
2.9	4.6	8.5	50	6.8	0.4	1.5	90
3.4	4.1	6.8	50	7.2	0.0		90
4.0	3.4	3.8	50				

While the vapor pressure-water content curve of a mixture may indicate the absence of hydrates, this evidence alone cannot be considered conclusive. That either rosaniline or p-rosaniline contains 4 molecules of water of crystallization does not seem likely, however, from other observations made in this Laboratory. For example, the highest percentage of water obtained in any sample prepared or purified was 7.2, against 17.9 required for 4 molecules (the calculations are based on an equimolecular mixture of rosaniline and p-rosaniline). If one of the components of the mixture contained 4 molecules of water of crystallization and the other was anhydrous, the amount of water present in an equimolecular mixture of the two should be approximately 8.5%. If this were the case, however, the vapor pressure-water content curve should show the breaks characteristic for hydrates. This it failed to do.

Erythrosin.—Erythrosin, or disodium tetra-iodo-fluoresceinate, has received much attention in the analytical work on food colors, because of the constant discrepancy in its analysis. Determinations of iodine in dried samples of this dye give results about 1% low, while those made on the pure acid agree very well with the theoretical value. Gomberg and Tabern¹³ found an average of 56.99% of iodine in the sodium salt (calc. for C₂₀H₆I₄O₅Na₂: 57.70), and of 60.67% (calc. for C₂₀H₅O₅I₄: 60.75) in the free acid. Their results for iodine content in samples of technical erythrosin were approximately 0.6% low. These investigators account for this discrepancy by assuming the presence of a small amount of water, equivalent to approximately 1 molecule, held very tenaciously. Similar conclusions have been reached by W. C. Holmes¹⁴ of the Color Laboratory in connection with a gravimetric method for determining erythrosin.

A vapor pressure-water content curve was obtained on a sample of re-

¹⁸ Gomberg and Tabern, J. Ind. Eng. Chem., 14, 1117 (1922).

¹⁴ Holmes, Estimation of Erythrosin, Color Trade J.

crystallized erythrosin containing 13% of water. No trace of hydrate formation was observed. (Table VI, Fig. 3, Curve C.) However, the sample which had been subjected to prolonged evacuation under pressure of less than 0.2 mm., and at a temperature of 160° , gave on analysis 56.58% of iodine, which agrees well with the value 56.55% required for a sample containing the equivalent of 1 molecule of water. Therefore, all work indicates that there must be an equivalent of 1 molecule of water in the sodium salt of erythrosin and that this water is bound much more firmly than ordinary water of crystallization.

			TABI	E VI			
			ERYTI	IROSIN			
H ₂ O removed %	H ₂ O to pure color ^a	Pressure Mm.	Temp.	$^{ m H_2O}_{ m removed}$	H ₂ O to pure color ^a	Pressure Mm.	Temp C.
1.2	13.65	21.5	50	9.4	4.1	2.0	50
2.2	12.4	16.8	50			21.1	90
3.3	11.2	12.8	50	10.4	3.0	12.0	90
4.3	10.0	9.0	-50	11.0	2.3	6.5	90
5.2	9.0	6.5	50	11.5	1.8	3.6	90
6.2	7.9	4.6	50	11.7	1.5	1.5	90
6.9	7.0	3.8	50	12.0	1.2	0.5	90
7.6	6.2	3.0	50			22.5	140
8.2	5.5	2.8	50	12.5	0.6	7.2	140
8.8	4.8	2.5	50	12.9	0.2	0.8	140
				13.0	0.0	• • •	140

Computed from water actually removed.

No definite evidence as to how this water is held is available at this time. Gomberg and Tabern¹³ suggest that the quinoid tautomer of the dye combines with water to give Formula I. This formula does not seem to explain the characteristics of this compound. There is no reason to expect a difference in structure between the sodium salt and the free acid which can easily be obtained in the anhydrous form. Pending further work on this subject, it is suggested that this seeming irregularity might be explained on the basis of an addition compound formed by the union of 1 molecule of the monosodium salt with 1 molecule of sodium hydroxide, such as shown in Formula II.

$$\begin{array}{c|c} I \\ ONa \\ \hline COONa \\ \hline I \\ \hline OH \\ \hline \end{array} \qquad \begin{array}{c} I \\ OH.NaOH \\ \hline COONa \\ \hline \end{array} \qquad \begin{array}{c} I \\ OH.NaOH \\ \hline \end{array}$$

Tartrazin, C₁₆H₉N₄S₂O₉Na₃: This is of especial interest as it is one of the 11 permitted food dyes. Anschütz¹⁵ records that tribarium tartrazin ¹⁵ Anschütz, Ann., 294, 288 (1897).

 $((C_{16}H_9N_4S_2O_9)_2Ba_3)$ contains 6 molecules of water. All investigators report that the di- and trisodium forms are anhydrous, although users of this dye know that the sodium salt very rapidly takes up approximately 17% of moisture on exposure to the air.

A pure sample of trisodium tartrazin was recrystallized from water and partially dried in the air. A moisture determination on this product showed approximately 33% of water. Vapor pressure-water content

TABLE VII

	. 00		TART	'RAZIN		. 0	
H ₂ O	———26 H ₂ O to			H ₂ O	3(H ₂ O to	,	
removed %	pure color	$_{ m Mols.}^{ m H_2O}$	Pressure Mm.		pure color	H ₂ O Mols.	Pressure Mm.
0.2	49.9	14.8	22.6	3.7	45.5	13.5	25.4
0.9	48.9	14.5	21.7	4.8	42.9	12.7	25.4
1.8	47.5	14.1	20.6	6.4	40.5	12.0	25.3
2.8	46.1	13.7	20.2	8.0	38.1	11.3	25.5
3.8	44.5	13.2	20.1	9.5	35.8	10.6	24.8
4.8	42.9	12.7	20.1	11.2	33.3	9.9	23.5
5.8	41.4	12.3	20.1	12.7	31.1	9.2	23.2
6.9	39.7	11.8	20.1	14.3	28.7	8.5	23.0
8.0	38.1	11.3	20.1	15.9	26.2	7.8	23.0
8.3	37.6	10.9	19.2	17.4	23.9	7.1	18.5
9.2	36.4	10.8	19.2	18.6	22.2	6.6	13.5
10.2	34.9	10.4	19.2	19.5	20.8	6.2	9.0
11.3	33.3	9.9	18.2	20.4	19.5	5.8	7.2
12.4	31.7	9.4	18.2	21.2	18.3	5.4	6.4
13.5	30.1	8.9	18.2	22.3	16.6	4.9	6.1
15.6	26.7	7.9	17.0	23.6	14.6	4.3	6.0
16.6	25.3	7.5	15.9	24.8	12.9	3.8	6.0
17.3	24.1	7.2	13.8	25.9	11.3	3.4	5.6
18.3	22.8	6.8	8.6	27.0	9.6	2.9	4.2
19.2	21.4	6.4	5.6	27.7	8.5	2.5	3.5
19.8	20.4	6.1	4.9	28.4	7.5	2.2	3.3
20.5	19.5	5.8	4.7	29.0	6.6	1.9	3.0
21.9	17.3	5.1	4.2	30.8	3.8	1.1	2.2
23.2	15.3	4.5	4.0	31.4	3.0	0.7	1.8
23.5	15.0	4.4	4.0	32.9	0.7	0.2	1.0
25.0	12.6	3.7		33.3	0.0	0.0	
25.8	11.3	3.4	3.8	••	• • •		• • •
26.6	10.3	3.0	3.6				• •
27.3	9.2	2.7	3.0	•			•••
28.2	7.9	2.3	2.9	••	•••	• • • •	• • •
28.5	7.3	2.1	2.7	• •	• • •		•••
29.2	6.3	1.9	2.5			• • •	* * * *
29.9	5.3	1.6	2.2		• • •	· · · · • • · ·	A
30.2	4.7	1.4	2.1		• • •	• • •	•••
33.3	0.0					• • •	•••

curves on this sample were obtained at 26° , and repeated at 30° because of certain irregularities observed at the lower temperature. Curves C

and D, Fig. 2, show that breaks in the curve obtained at 26° occur at points corresponding to hydrates of 14, 11, 10, 6 and 3 molecules of water. As the presence of the hydrates containing 10 and 11 molecules of water seemed a little doubtful, owing to the slight change in pressure (1 mm.) between them and the next higher hydrate, and in order to obtain more information regarding the location of the curve between the hexa- and octahydrate, this experiment was repeated at 30°. The curve obtained at the higher temperature indicates the presence of hydrates containing 14, 10, 6 and 3 molecules of water. The rounding-off effect due to the presence of higher hydrates in the interior of the particles, as suggested by Beutell and Blaschke, is clearly demonstrated between the decaand hexahydrates which differ in pressure by 13 mm.

As already mentioned, tartrazin after exposure to air contains about 17% of water. This corresponds to the hexahydrate, which has a vapor pressure approximately that of the aqueous tension of the air.

Summary

Vapor pressure-water content curves have been obtained for methylene blue, crystal violet, erythrosin, magenta and tartrazin, for the purpose of determining whether the water present in these dyes is adsorbed or held as water of crystallization. Crystal violet and tartrazin alone show hydrate formation. Further proof was also obtained that the equivalent of 1 molecule of water in crythrosin is present as part of the molecule and a new theory of the structure of this dye is offered.

WASHINGTON, D. C.

[Contribution from the Chemical Laboratory of the University of Illinois]
THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. III. THE
DETERMINATION OF BROMATE IN THE PRESENCE OF FERRIC
IRON

By G. FREDERICK SMITH Received April 27, 1923

In the former papers of this series, the stability of boiling solutions of potassium bromate in the presence of mineral acids was demonstrated and the relation of this stability to further applications in the use of bromate for volumetric analysis suggested. The use of bromate in acid solution in the presence of mercuric ion was shown to alter the course of several reactions of analytical importance, increasing the oxidation value of the bromate from 5 to 6 equivalents of oxygen, thus preventing the trouble-some formation of free bromine and in other ways increasing the flexibility and value of bromate oxidimetric processes.

Determinations involving the use of bromic acid in excess generally ¹ This Journal, 45, 1115, 1417 (1923).

involve the determination of this excess in the presence of ferric iron. The most common procedure consists in adding potassium iodide to the acid solution followed by a determination with thiosulfate solution of the iodine liberated. Ferric iron, therefore, interferes through the simultaneous liberation of iodine. Methods employed for preventing this influence of ferric iron in iodimetric estimations of strong oxidizing agents, have been devised. The object of the present paper is not only to demonstrate how these known methods may be improved and adapted to the determination of bromates, but also to introduce entirely new reactions for the determination of bromate in the presence of ferric iron.

These reactions, which proceed in the presence of mercuric ion in accordance with the principles stated in the second paper of this series, employ pure sodium oxalate and standard ferrous sulfate solutions in excess as reducing agents, and the excess is determined by titration with standard permanganate in the usual manner. The reactions follow: (1) $3H_2C_2O_4 + KBrO_3 \rightarrow 6CO_2 + KBr + 3H_2O$; (2) $6FeSO_4 + KBrO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + KBr + 3H_2O$.

Previous Work

Iodimetric determinations in the presence of ferric iron involve the formation of complex ferric salts which do not give ferric ions in solution and which consequently do not act on potassium iodide. Phosphoric acid thus converts ferric salts to complex salts containing the diphosphatoferric ion, $(Fe(PO_4)_2)^{---}$. Sodium pyrophosphate in excess dissolves ferric phosphate to give a colorless solution according to the same principle. Other reagents likewise form complex salts with ferric iron which do not give reactions of the ferric ion. Phosphoric acid and phosphate complexes only are of importance here.

Moser² determined copper iodimetrically in the presence of iron by the addition of an excess of sodium pyrophosphate to a solution of copper sulfate and ferric chloride with the formation of cupric and ferric pyrophosphates, of which the copper precipitate was readily soluble and the ferric precipitate difficultly soluble in the excess employed. The solution was then treated with an excess of potassium iodide, acidified with acetic acid and the iodine liberated after 10–15 minutes by the action of the copper alone, was titrated with sodium thiosulfate. This process is objectionable because of the time required for the liberation of iodine, the difficult solubility of ferric pyrophosphate in the excess of pyrophosphate, and the limitation in the amount of ferric iron that may be present without interference.

The action of phosphoric acid in preventing the liberation of iodine from potassium iodide by ferric iron was used by Barnebey³ in the iodimetric determination of iodate. The similar determination of permanganate iodimetrically was carried out by Barnebey and Hawes.⁴ In general the methods involving these processes limit the amount of iron permissible without measurable interference.

² Moser, Z. anal. Chem., 43, 597 (1904).

³ Barnebey, This Journal, 37, 1502 (1915).

⁴ Barnebey and Hawes, ibid., 39, 607 (1917).

Factors Influencing the Determination of Bromate Iodimetrically

The best procedure for the iodimetric determination of bromates should be one which works advantageously in the presence of the largest amount of iron. At the same time conditions must be chosen which require a minimum length of time in the reaction between the bromate to be determined and the iodide added. The method finally devised combined the principles of the phosphoric acid process of Barnebey and the pyrophosphate method of Moser.

With increasing amount of iron in phosphoric acid solution the ferric iron color of the solution increases regardless of increasing concentration of phosphoric acid. That this color is due to the presence of ferric ions formed by the dissociation of the diphosphato-ferric ion may be shown by the liberation of iodine from potassium iodide added to such solutions. To prevent this dissociation from giving ferric ions the phosphate ion

2.6 H₃PO₄ — Ba(BrO₃)₂ — KI

2.2 Constants

1.8 Ba(BrO₃)₂ = 0.0 b 96 c.

EQUIV. KI = 1.0 to 1.5 g.

N. Volume = 100 cc.

1.0 0.6 cc. 0.1 M. Na₂S₂O₅

Fig. 1

must be added in large excess. This was done by adding easily soluble sodium pyrophosphate.

The addition of sodium pyrophosphate to a phosphoric acid solution greatly decreases the hydrogen-ion concentration. Under these conditions even strong oxidizing agents such as chromic acid fail to liberate iodine rapidly upon the addition of potassium iodide. The very high oxidizing power of bromic acid, however, overcomes this disadvantage. The time rate of oxidation of potassium iodide to free iodine by potassium dichromate with various concentrations of phosphoric acid has been determined by Barnebey.⁵

To show the comparative oxidizing power of bromic acid for potassium iodide a curve was constructed showing the equilibrium between barium bromate, potassium iodide and phosphoric acid in the presence of increasing concentrations of phosphoric acid; in the experiments, 1 minute and 3 minutes were allowed as reaction periods. The results are shown in Fig. 1.

The values were obtained as follows. The measured volume of barium bromate solution was diluted with water, the proper amount of phosphoric acid to give the acid normality shown (calculated on the basis of 3 available hydrogen atoms) was added and the whole diluted to 90 cc.; 1 to 1.5 g. of potassium iodide dissolved in 10 cc. of water was added and the mixture stirred vigorously during the allotted time for reaction, whereupon the

⁵ Barnebey, This Journal, 39, 604 (1917).

liberated iodine was titrated with approximately $0.1\ N$ sodium thiosulfate solution. When the reduction of the bromate by potassium iodide was incomplete at the time the thiosulfate was added, part of the thiosulfate was oxidized slightly. The extent of this reaction was negligibly small in all cases.

By comparison with the data of Barnebey for the corresponding dichromate reaction it will be seen that for $2\,N$ phosphoric acid the reduction of barium bromate is complete in 1 minute as compared with 3 minutes required by the dichromate reaction. Allowing 3 minutes as reaction period, complete reduction of bromate takes place in a little less than N phosphoric acid as compared with $2\,N$ acid required by the dichromate reduction. The strength of bromic acid under these conditions compared with that of chromic acid as an oxidizing agent for iodides is, therefore, roughly 3 to 1. It is thus assured that, without increase of the time in the reactions involved, the hydrogen-ion concentration of phosphoric acid may be decreased by the addition of considerable sodium pyrophosphate.

The Effect of Sodium Pyrophosphate in Phosphoric Acid Solution Upon the Formation of an Undissociated Diphosphato-Ferric Ion Complex

As has been shown in previous papers of this series, solutions of nitric and perchloric acid are best adapted to the determinations involving bromate oxidations. Solutions containing ferric perchlorate of increasing iron content were treated with phosphoric acid in different concentrations and diluted to 100 cc. Proportionate amounts of crystalline sodium pyrophosphate were then dissolved in these solutions, followed by the addition of 1-1.5 g. of crystalline potassium iodide. The potassium iodide was dissolved by vigorous stirring to prevent high local concentrations of dissolved material and the reaction medium was allowed to stand in covered beakers for 30 minutes. At the end of this time starch indicator was added and the iodine which had been liberated was titrated with 0.1 N sodium thiosulfate. A blank determination, under the same conditions without iron, was made to show the effect of atmospheric oxygen in liberating iodine from the iodide added. Under conditions which were least favorable to the rapid reduction of bromate by potassium iodide, the time required for the completion of the reaction between 25.00 cc. of 0.1 N potassium bromate and excess of potassium iodide was also determined. The results of the experiments are shown in Table I.

As will be seen, iron to the extent of 600 mg. may be effectively eliminated as an interference in iodimetric determinations of bromates. Substantially the same results were obtained using crystalline ferric nitrate instead of ferric perchlorate. When ferric sulfate solutions are employed, much more iron may be present without interference, as shown by Barnebey. The first and second experiments in Table I show that under

similar conditions without the addition of sodium pyrophosphate a prohibitive error is introduced with but half the amount of ferric iron possible with addition of pyrophosphate. In all the above experiments, the solutions remained clear throughout the whole of the time interval employed.

TARLE I

THE ACTION OF FERRIC IRON UPON POTASSIUM IODIDE IN PHOSPHORIC ACID SOLUTION
AS INFLUENCED BY SODIUM PYROPHOSPHATE

Iron was added as ferric perchlorate (containing 11% of Fe) free from ferrous iron. Time of reaction, 30 minutes. Volume of solution, 100 cc. The sodium pyrophosphate did not liberate or absorb iodine under the conditions studied. 1.0 g. of potassium iodide was added in the first five experiments and 1.5 g. in the last six.

Amount of Fe	Cone. H ₃ PO ₅	Na ₄ P ₂ O ₇ 10 H ₂ O added G.	0.1 N Na ₄ S ₂ O ₃ ⁿ required Ce.	Blank without Fe. Ce. of thio- sulfate	Time required to: KBrO ₃ + KI reaction Same conditions Min.
0.2	2.0	None	0.25		
.3	$^{2.0}$	None	.51		
.2	1.0	3.0	.04		
.3	1.5	3.0	.11	0.01	
.3	1.5	4.0	.08	none	<3
.4	2.0	4.0	. 56		
.4	2.0	6.0	.20	0.01	<3
.5	2.0	5.0	.50		
.5	2.0	6.0	.34		
.5	2.0	8.0	.25	0.01	
. 6.	2.0	10.0	.20	0.00	<3

^a 1/10 of these values is the extent of their effect in practice.

The iodine liberated from potassium iodide by 25.00 cc. of $0.1\ N$ potassium bromate in $0.3\ N$ hydrochloric acid solution required 26.21 cc. of the sodium thiosulfate used in Table I. With $0.66\ M$ phosphoric acid 26.21 cc. also was required. With $2\ M$ phosphoric acid 26.15 cc. was required. With $2\ M$ phosphoric acid to which $10\ g$. of sodium pyrophosphate decahydrate per 100 cc. had been added, 25.99 cc. of the sodium thiosulfate solution was required. Therefore, the sodium thiosulfate in strong phosphoric acid solution with and without the addition of sodium pyrophosphate should be standardized, using potassium bromate under the same conditions.

The procedure for preparing a nitric or perchloric acid solution containing ferric iron for determination of its bromate content consists, therefore, in adding sodium bicarbonate to neutralize the acid and give a small precipitate, followed by phosphoric acid or phosphoric acid and sodium pyrophosphate, depending upon the amount of iron present, and finally 1–1.5 g. of potassium iodide with stirring. After 2 to 3 minutes the liberated iodine is titrated with standard thiosulfate using starch as indicator. The thiosulfate should be standardized under the same conditions.

The Determination of Bromates with an Excess of Pure Sodium Oxalate Followed by Permanganate Determination of this Excess

Since many oxidation processes involving bromates are best conducted at 100°, iodimetric determination of any excess of bromate can be made only after the solutions have been cooled to room temperature. It would, therefore, be an advantage to develop a method for bromate determination applicable to hot solutions, and Reaction 1 was accordingly studied.

An exactly $0.1\ N$ solution of sodium oxalate and approximately $0.1\ N$ solutions of potassium and barium bromate were prepared; $25.00\mathrm{cc}$. portions of the latter solutions were treated with $0.1\ N$ mercuric perchlorate solution in amount slightly more than that equivalent to the bromide ion resulting from the subsequent reduction of the bromate, and $50.00\ \mathrm{cc}$. of the $0.1\ N$ sodium oxalate solution was added followed by 5 cc. of 95% sulfuric acid, and the volume was adjusted to $100\ \mathrm{cc}$. The solution was boiled for 3 minutes in a covered beaker and, without cooling, the excess of sodium oxalate was titrated with potassium permanganate solution that had been standardized against pure sodium oxalate.

The standardization of three bromate solutions in this way was accomplished with the results listed in Table II.

TABLE II

STANDARDIZATION OF POTASSIUM AND BARIUM BROMATE SOLUTIONS WITH SODIUM OXALATE IN SULFURIC ACID SOLUTION FOLLOWED BY DETERMINATION OF THE EXCESS OF OXALATE WITH POTASSIUM PERMANGANATE

Fixed quantities: 25.00 cc. of approximately 0.1 N KBrO₃ or Ba(BrO₃)₂; 50.00 cc. of 0.1000 N Na₂C₂O₄; 5 cc. of 95% H₂SO₄. 7–10 cc. of 0.1 N Hg(ClO₄)₂ in 0.1 N HClO₄ solution. Volume of solution, 100 cc. Time of boiling, 3 minutes.

Sample	0.10040 N KMnO ₄ required Cc.	Bromate determined N	Bromate using pure As ₂ O ₂ N	Difference
1 KBrO ₃	24.97	0.09971	0.09965	+0.00006
$Ba(BrO_3)_2$	25.125	.09909	.09903	+ .00006
2 KBrO ₃	24.08	.09972	.09973	00001

These results are in each case the means of at least three closely agreeing determinations. The potassium bromate from a measured portion of Sample 2, after reduction with hydrazine, was precipitated with excess of silver nitrate and the weight of the silver bromide gave the closely agreeing value, $0.09967\ N$. The purity of the arsenious oxide used was thus proved.

The end-point in the titrations of Table II in which permanganate was used is the equal in permanency to the ordinary sodium oxalate-permanganate titration in spite of the presence of considerable mercuric bromide, but the last 3 or 4 drops of permanganate added are only slowly reduced. The point at which the pink color produced is permanent for $^3/_4$ to 1 minute is the true end-point of the reaction.

The explanation of the influence of mercury in the determinations given

- ⁶ Sodium oxalate solutions should be made up as used to avoid decomposition which occurs upon standing.
- ⁷ It was found that the pink color from 1 drop of 0.1 N permanganate in excess often persisted after 12 hours or even longer.

in the second article of this series was further tested by substituting $0.1\,N$ silver sulfate solution for mercuric perchlorate, and using a considerable excess. The concentration of the solution of Sample 2 potassium bromate was thus found to be $0.09974\,N$. The silver bromide precipitated during the reaction was without effect on the end-point. The addition of mercuric perchlorate solution to these reactions may be readily obviated through the use of mercuric bromate as standard solution. The use of mercuric bromate for this purpose will be considered in subsequent papers of this series.

Sodium oxalate serves as one of the very best standards of quantitative analysis.⁸ The standardization of bromate solutions with sodium oxalate as the only reference reagent, according to the determinations included in Table II, thus shows that bromate is probably the equal of permanganate in accuracy as a standard in volumetric analysis.

The standardization of bromate solutions by comparison with pure arsenious oxide or pure metallic antimony, following the procedure of Györy⁹ and more recently the modified Györy electrometric method of Zintl and Wattenberg¹⁰ further increases the value of bromate for volumetric processes. The high purity of metallic antimony available for this purpose has been described by Henz.¹¹ That it dissolves in hot concd. sulfuric acid to give only trivalent antimony was shown by Osterheld and Honegger.¹² Work now being carried out in another laboratory,¹³ involving the use of potassium bromate and including a critical study of its physical properties as related to stability will further increase the value of bromate as a standard.

By the use of bromate solutions standardized against sodium oxalate and potassium permanganate to liberate iodine from potassium iodide in acid solution, sodium oxalate can in general be used in place of arsenious oxide as a primary standard for iodimetric processes with no sacrifice in accuracy or convenience. Another method in which sodium oxalate is used as primary standard was devised by Rosenthaler.¹⁴

Factors governing the determination of bromate in the presence of ferric iron by the oxalate-permanganate method given above are shown in Table III.

It will be seen from Table III that solutions containing only free sulfuric acid serve for oxalate reduction of bromate in hot solution in the presence of mercuric perchlorate. Phosphoric acid, if added to decolorize

⁸ Sörensen, Z. anal. Chem., 42, 352, 512 (1903); 45, 272 (1906).

⁹ Györy, Z. anal. Chem., 32, 415 (1893).

¹⁰ Zintl and Wattenberg, Ber., 56, 472 (1923).

¹¹ Henz, Z. anorg. Chem., 37, 1 (1903).

¹² Osterheld and Honegger, Helv. chim. acta, 2, 398 (1919).

¹³ Private communication.

¹⁴ Rosenthaler, Z. anal. Chem., 61, 219 (1922).

the iron present, should be added just before titration or, better, at the end of the titration with permanganate. The preparation of the nitric or perchloric acid solution of a bromate containing ferric iron for determination of its bromate content is, therefore, the same as that for iodimetric

TABLE III

THE DETERMINATION OF POTASSIUM BROMATE WITH AN EXCESS OF SODIUM OXALATE IN SULFURIC, PHOSPHORIC AND PERCHLORIC ACID SOLUTIONS IN THE PRESENCE OF MERCURIC PERCHLORATE

Fixed quantites: 25.00 cc. of 0.09973 N KBrO₃; 50.00 cc. of 0.1000 N Na₂C₂O₄; 10 cc. of 0.1 N Hg(ClO₄)₂ in 0.1 N HClO₄. Reaction volume, 100 cc. Time of boiling, 3 minutes. Theoretical KMnO₄ for excess of Na₂C₂O₄, 26.18 cc.

Acid used	Other ma G.	terial present Salt	Amount KMn(used Cc.	Difference from calc. Cc. KMnO
	G.	Gait	Cc.	Cc. KMIIO
3 95% H ₂ SO₄+ \			26.35	+0.17
3 85% H₃PO₄ ∫	• • •		20.00	70.17
10 60% HC1O ₄	0.1	Ferric iron	26.33	+0.13
	5	NaClO ₄ .H ₂ O	26.21	+0.03
E 0507 TT 00	5	KNO ₃	26.20	+0.02
5 95% H ₂ SO ₄			26.20	+0.02
	0.1	Ferric iron ^a	$\{ 26.20$	+0.02
			26.21	+0.03

^a 3 cc. of 85% H₃PO₄ added just before titration with permanganate.

determination, addition of sulfuric acid following neutralization, in place of phosphoric acid and sodium pyrophosphate. The effect of more than 3 minutes' boiling was not tested when using phosphoric or perchloric acid instead of sulfuric acid.

The Determination of Bromate in the Presence of Mercuric Salt Using Ferrous Sulfate Followed by Titration of the Excess with Permanganate Solution

A second substitute for the iodimetric determination of bromates, using standard ferrous sulfate and potassium permanganate solutions, following the second reaction given above, would prove highly desirable if accurate because, as in the oxalate and iodimetric methods already described, the standard solutions used are the common stock reagents of any analytical laboratory. The determinations of bromates by this reaction would be most convenient if they could be made applicable in the presence of nitric, perchloric and phosphoric acid solutions, since bromate oxidation processes are best carried out in the presence of the two former acids, and phosphoric acid could be used to decolorize the ferric iron, giving a sharper permanganate end-point.

Standard solutions of potassium permanganate and ferrous sulfate were prepared in the usual manner by comparison with each other and with pure sodium oxalate. Potassium bromate was standardized with pure arsenic trioxide. Measured amounts of potassium bromate solution were treated with an excess of the equivalent amount of mercuric perchlorate solution and a considerable excess of standard ferrous sulfate solution was added. In the presence of $0.5\ N$ nitrie, perchloric and sulfuric acids complete reduction of the bromate was obtained in 2 to 3 minutes at room temperature. Molar phosphoric acid gave the same time of reduction. The results are listed in Table IV.

TABLE IV

THE DETERMINATION OF POTASSIUM BROMATE USING FERROUS SULFATE AND POTASSIUM PERMANGANATE IN PRESENCE OF MERCURIC PERCHLORATE

Fixed quantities: 25.00 cc. of $0.09803~N~{\rm KBrO_3}$; 25–30 cc. of $0.1~N~{\rm Hg(ClO_4)_2}$ in $0.1~N~{\rm HClO_4}$; 50.00 cc. of $0.09412~N~{\rm FeSO_4}$ in $0.1~N~{\rm H_2SO_4}$. Dilution to 150 cc. 2–3 minutes allowed for reduction of ${\rm KBrO_3}$. 24.24 cc. of $0.09404~N~{\rm KMnO_4}$ required for theoretical excess of FeSO₄.

Acid	Equiv. norm. of acid	0.09303 N KMnO ₄ required Cc.	Difference from calc. Cc. of KMnO ₄	Aeid	Equiv. norm. of acid	0.09303 N KMnO ₄ required Cc.	Difference from cale, Cc. of KMnO ₄
	(0.5	24.22	-0.02	TINIO	$\int 0.25$	24.06	-0.18
	0.5	24.24	=0.00	HNO_3	0.5	24.05	-0.19
HClO ₄	$\{0.5$	24.22	-0.02		1.0	24.24	± 0.00
	1.0	24.24	=0.00	${ m H_3PO_4}$	$\{1.0$	24.21	-0.03
	1.0	24.27	+0.03		(1.0	24.21	-0.03
	0.25	24.07	-0.17				
H ₂ SO ₄	0.5	24.07	-0.18				
112504	0.5	24.03	-0.21				
	1.0	24.02	-0.22				

Phosphoric acid sufficient to decolorize the iron present was added at the end-point in all these experiments if not already present.

From Table IV it is seen that the experimental and theoretical results obtained agree excellently in the case of phosphoric and perchloric acid solutions but are uniformly in error for nitric and sulfuric acid solutions. The end-point is best and most permanent in phosphoric acid solution but is very satisfactory as well in perchloric acid solution. As with a permanganate-oxalate end-point in the presence of mercuric salt, the last few drops of permanganate added are but slowly reduced and the pink tinge should persist for $^3/_4$ to 1 minute while the solution is stirred. The explanation of the error with nitric and sulfuric acid solutions is not apparent and is unusual in its constancy. The study of the electrometric end-point as applied to the reaction will be considered later in connection with work on volumetric processes involving bromate solutions, but the slowness of the reaction at the end-point would probably interfere with this method.

The preparation of bromate solutions in nitric acid containing ferric iron for determination of their bromate content according to the procedure of Table IV is the same as that for the iodimetric determination and the oxalate procedure already given.

The results here reported were obtained with mutually calibrated flasks, burets and pipets and are believed to be accurate to ± 0.02 cc.

Summary

The determination of bromates in the presence of ferric iron was studied, three methods proposed and their applicability demonstrated experimentally.

- 1. Iodimetric Method. Phosphoric acid solutions containing sodium pyrophosphate in which the dissociation of the resulting iron complex to give ferric ions is less than in the presence of either reagent alone, were analyzed for their content of bromate by the addition of potassium iodide in excess and titration of the liberated iodine with sodium thiosulfate. The time rate of reduction of bromate by potassium iodide with various concentrations of phosphoric acid was determined. The necessary variation in the concentration of phosphoric acid and sodium pyrophosphate with increasing amounts of ferric iron was determined.
- 2. Oxalate-Permanganate Method. The bromate was reduced by excess sodium oxalate in boiling sulfuric acid solution in the presence of mercuric perchlorate and the excess oxalate determined by titration with potassium permanganate. It was shown that this reaction furnishes the basis of an improved method for iodimetric standardization using sodium oxalate as primary standard.
- 3. Ferrous Sulfate-Permanganate Method. This involved the same procedures as in the Oxalate-Permanganate Method except that ferrous sulfate was substituted for sodium oxalate and titration was effected cold instead of in a hot solution.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF McGILL UNIVERSITY]

OXONIUM COMPOUNDS IN THE VAPOR STATE. METHYL ETHER—HYDROGEN CHLORIDE

By O. Maass and D. M. Morrison Received May 2, 1923

Organic compounds containing oxygen have been shown to form complexes with the halogen hydrides; these are known as oxonium compounds. For reasons which are discussed below, further work dealing with their stability is of interest. In the investigation which is the subject of this paper, methyl ether and hydrogen chloride were mixed in the gaseous state with the object of determining whether or not association of these molecules occurred.

A thorough investigation of oxonium compounds has been made by D. McIntosh¹ and some of his co-workers. In one of his papers² on the sub-

¹ McIntosh, This Journal, 27, 26, 1013 (1905); 33, 71 (1911).

² Ibid., 34, 1273 (1912).

ject, properties of these compounds were reviewed with the object of comparing the oxonium complexes with the so-called molecular compounds such as water or alcohol of crystallization. The conclusion arrived at was that these oxonium compounds were very stable. They are simple, that is, generally 1 molecule of organic liquid unites with 1 molecule of acid. The melting points of the compounds are far above the melting points of the constituents; also, the behavior on electrolysis and the magnitude of the heats of formation serve to distinguish the oxonium compound from the ordinary solvent of crystallization.

The existence of these compounds is definitely established in the solid state; as they melt, dissociation into the original molecules takes place. Conductivity experiments indicated that this was not at all complete, but the validity of this derived interpretation is not absolutely certain. If it could be definitely shown that a measurable amount of association exists in the liquid or gaseous state, the character of the oxonium compound would at once be established as comparable to that of ammonium chloride.

This is of particular interest since in the past the structure of the oxonium compound has been given by assigning a valence of 4 and in some cases 6 to the oxygen atom; this is not in agreement with the present theory of the structure of the atom and consequent ideas of valence.

Methyl ether and hydrogen chloride form an oxonium compound melting at -96° ; the liquid boils lower than -12° . It is, therefore, possible to mix these two as gases above this temperature. The methyl ether and hydrogen chloride were prepared and purified as previously described and the boiling points were shown to be in exact agreement with those previously found.

The experimental procedure consisted in mixing a definite volume of hydrogen chloride with an equal volume of methyl ether in a container having exactly twice this volume. The pressures of the unmixed hydrogen chloride and methyl ether were the same; hence, after the gases were mixed any decrease in pressure would indicate association or increase in molecular attraction; which of these two would be the cause of the change, if any took place, would then be established in the manner described further on.

The accompanying diagram (Fig. 1) will serve to illustrate the manner in which the required amounts of methyl ether and hydrogen chloride were mixed.

The hydrogen chloride was condensed in the bulb M; the pressure tap L made it possible to keep it liquid at the temperature of a mixture of solid carbon dioxide and ether. The construction of this tap is shown in the diagram. The stopper, of large

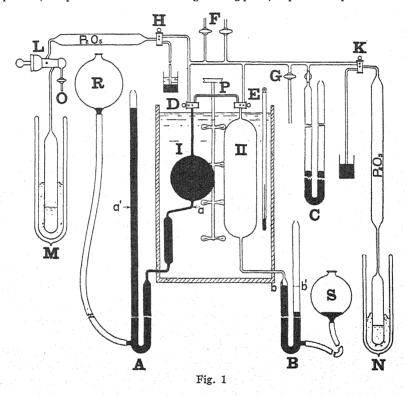
³ This Journal, 35, 535 (1913).

⁴ Ref. 2, p. 1279.

⁵ This Journal, 44, 1709 (1922).

diameter, is surrounded at the bottom by a space which may be evacuated and then closed off by means of the tap O, thus being held in place by the pressure of the atmosphere. The area exposed to atmospheric pressure in this way is large as compared to that exposed to the vapor pressure of the hydrogen chloride and taking into account the angle at which this latter pressure is applied, some 30 atmospheres' pressure in the bulb may be withstood, yet the stopper turns easily. The tap L is connected through a pentoxide tube and the 2-way tap H to the main apparatus. The volumes up to the tap H could be swept out as indicated in the diagram.

The methyl ether was condensed in Bulb N which is similarly connected to the main apparatus, except that on account of its high boiling point, no pressure tap was necessary.



Two reservoirs, I and II, were contained in a bath, the temperature of which could be kept constant. Each reservoir was connected to a manometer (A and B, respectively) in which the mercury could be raised or lowered. These reservoirs were connected through 2-way taps, D and E, to the glass-tube system which could be evacuated through Taps F and filled with air through Tap G. The volumes of I and II were chosen such that II measured from Point b was exactly twice that of I measured from Point a. This was tested by completely evacuating I and II, filling I with air at atmospheric pressure, and sending this into II, through the capillary tube P by raising Reservoir R until the mercury filled I up to Tap D. This was repeated, while the temperature was kept constant, and it was found that the mercury in both arms of manometer B was level when it reached the height b. Obviously with this procedure no corrections need be applied to the gas laws.

is approached and the aberrations from the gas laws of this mixture will mask any effect due to association of the molecules.

It might be argued that all the diminutions in pressure when the gases are mixed might be due to a similar cause; whether or not this is the case can be tested in the following manner. The concentration of the hydrogen chloride in the mixture is n(1-X)/2v, that of the methyl ether n(1-X)/2v, and that of the oxonium compound nX/2v; hence, if the above equilibrium between oxonium compound, methyl ether and hydrogen chloride really exists.

$$\frac{n \ (1-X)^2}{2nX} = K \tag{2}$$

where K is a constant

Substituting $\frac{Pv}{RT}$ for n

$$\frac{P(1-X)^2}{X} = 2 RTK = k (3)$$

where k is a constant at a definite temperature.

Hence X and consequently p (Eq. 1) can be calculated for various value of P and this value checked by experiment.

Table II

EXPERIMENTAL DATA AND CALCULATED AND OBSERVED VALVES OF P

Temp.	Press. HCl P ₁ mm.	Press. $(CH_3)_2O$ P_2 mm.	X Calc.	Press. of mixt. Calc. p mm.	Press. of mixt. Found	Differ- ence
18.8	756.0	756.0	0.1124		713.53	
	573.4	573.4	.0896	547.8	547.5	+0.3
	382.9	382.9	.0634	368.8	369.2	-0.4
9.2	758.0	758.0	.1472		702.2	
	557.0	557.0	.1162	524.7	524.4	+0.3
	378.7	378.7	.0848	362.65	362.7	-0.05
	218.4	218.4	.0524	212.7	212.5	+0.2
	767.8	385.5		546.1	545.2	+0.9
	382.1	758.5		540.2	539.8	+0.4

The first experiments carried out at 18.8° show agreement within experimental error between calculated values and those found. The calculation was based on the value of k at 18.8° and atmospheric pressure. See Table I.

Furthermore, the test of varying the relative proportions of the gases to be mixed was applied. In this case p can be calculated as follows.

Let P_1 equal the pressure of unmixed hydrogen chloride of which there are N_1 gram molecules in volume v_i let P_2 be the pressure of unmixed methyl ether of which there are N_2 gram molecules in volume v.

Then, if N_3 gram molecules of oxonium compound are formed.

$$\frac{\frac{(N_1 - N_3)}{(2v)} \frac{(N_2 - N_3)}{(2v)}}{\frac{N_2}{2v}} = K \tag{4}$$

where K is identical with K in Equation 2.

$$N_1 = \frac{P_1 v}{RT} \qquad N_2 = \frac{P_2 v}{RT}$$

$$(N_1 + N_2 - N_3) = \frac{2 p v}{RT}$$

$$\therefore N_3 = \frac{P_1 v}{RT} + \frac{P_2 v}{RT} - \frac{2 p v}{RT}$$

and substituting for N_1 N_2 N_3 in Equation 4,

$$\frac{(2p - P_2)(2p - P_1)}{(P_1 + P_2 - 2p)} = 2RTK = k$$
 (5)

The next series of experiments was carried out at 9.2°. The pressure change on mixing the gases (56.0 mm.) is greater than at the higher temperature and, therefore, the experimental error is correspondingly smaller. The very good agreement between calculated and observed values shows that the assumption of the equilibrium in which there is a 1:1 compound is without doubt correct⁶ and the result is not due to the mass effect of changed molecular attraction in the gas mixture.

As was mentioned above, at temperatures below -4° , the condensation temperature (boiling point) of the mixture being near, the molecular attractions play a part as well as association in causing a diminution in pressure when the gases are mixed. At -7.65° the above calculation should, therefore, not be valid because the association X is really smaller than that calculated from the diminution of pressure, and hence the diminution calculated on this basis for a lower pressure of unmixed gases will be smaller than that observed. An experiment was carried out at this temperature in which the original pressures of hydrogen chloride and methyl ether were 383.2 mm. of mercury. The pressure observed on mixing was 363.0 mm., whereas that calculated on a basis neglecting molecular attraction was 331.5.

The conclusion which may be drawn from all of these experiments is that methyl ether and hydrogen chloride form an oxonium compound, $(CH_3)_2O.HCl$, existing in the vapor state to a measurable extent even at temperatures 150° above its melting point. The compound is quite analogous to ammonium chloride which also is partly dissociated into its component molecules when it is vaporized.⁷

In the latter case, 2 polar molecules form the resultant compound. Methyl ether is not polar, that is, in the sense that the center of gravity of the positive and negative electricity is identical when the molecule is built up out of atoms to which the Langmuir or Thomson electron structure is given. Although this is in agreement with its dielectric constant, the

⁶ At 9.2° and 758.0 mm. pressure the decrease in pressure on mixing is 55.8 mm. Hence, at half the initial pressure, 378.7 mm., one might have expected half the above decrease in pressure 27.9 mm., but the decrease in pressure found was 16.0 mm. which is in perfect agreement with the calculated change (See Table II).

⁷ Smith and Lombard, This Journal, 37, 38 (1915).

stability of the oxonium compound is rather surprising. However, from the space model it can be imagined that the approach of the hydrogen end of the very polar hydrogen chloride molecule to the oxygen of the methyl ether might induce pronounced polarity in the latter. This would mean a displacement of the methyl groups and the attachment of a hydrogen nucleus to the oxygen atom quite in agreement with the electrolytic dissociation of the oxonium compound when in solution. Furthermore, the oxonium compound itself would be polar, which would account for the higher complexes² [(CH₃)₂O.3HCl] which have been isolated at low temperatures.

It will be interesting to investigate other oxonium compounds in this manner. The compound formed between ether and chlorine is particularly interesting, since in this case neither of the component molecules is itself polar in the above sense. This compound, therefore, should not be detectable in the gaseous state.

In this connection it may be pointed out that the chlorine complexes when melted are non-conductors, that is, no electrolytic dissociation occurs.

The heat of formation of methyl ether-hydrogen chloride can be calculated from the above experimental data, but this will be left until other oxonium compounds have been examined.

Acknowledgment is hereby made of a scholarship granted during the time of this research by the Honorary Advisory Council for Scientific and Industrial Research of Canada.

Summary

Equal volumes of methyl ether and hydrogen chloride were mixed in the gaseous state at atmospheric pressure and the resultant pressures recorded over the temperature range 30° to -10°. From these data the amount associated to form the oxonium compound, (CH₃)₂OHCl, was calculated, and the resultant pressures on mixing these gases, at pressures other than atmospheric and in unequal proportions, were deduced. These latter were checked by observation, thus proving the original assumption to be correct, namely, that a 1:1 compound exists in the vapor state, the dissociation of which increases with rising temperature.

The similarity between methyl ether-hydrogen chloride and ammonium chloride has been pointed out and the formation of the former attributed to induced polarity in the methyl ether molecule caused by the polar hydrogen chloride molecule.

MONTREAL, CANADA

[CONTRIBUTION FROM THE DEVELOPMENT LABORATORIES OF THE HAWTHORNE WORKS, WESTERN ELECTRIC COMPANY, INC.]

THE SYSTEM, LEAD-ANTIMONY

By R. S. DEAN Received May 3, 1923

Introduction

The equilibrium in the system, lead-antimony, because of the commercial importance of this series of alloys, has been the subject of a very considerable number of investigations. The conclusion reached in most of them and generally accepted in all the recent handbooks and texts¹ is that neither solid solutions nor compounds are formed at least in the alloys rich in lead.

The earliest investigation of the system seems to have been made by Roland-Gosselin2 who found by thermal investigations that the system was a simple eutectiferous one with the eutectic containing about 12.5% antimony and melting at 228°. This eutectic temperature was checked roughly by Ewen.3 Stead,4 however, in a thermal and microscopic examination of the system found a eutectic temperature of 247°, but his microscopic examinations confirmed the earlier conclusion that the system was simple eutectiferous. Campbell⁵ with very little further data accepts Roland-Gosseliu's results. In 1907 Gontermann⁶ reviewed the conflicting data and made a very careful thermal investigation of the system. In general his results checked those of Stead. It is to be noted, however, that with allows above 13% Gontermann obtained two arrests for the eutectic point. He explained this as a matter of crystal size, which explanation, however, has been questioned by Guertler who leaves the facts unexplained. Gontermann further found no detectable arrest in the cooling curve for 1% antimony alloy, but since his microscopic examination of the specimens showed dendrites he discarded the possibility of the formation of solid solution. The later investigations of Loebe⁷ and of Leroux8 have agreed quite closely with those of Gontermann.

A number of investigations of the physical properties of the lead-antimony alloys have been made from which conclusions have been drawn regarding the equilibrium. The potential of the lead-antimony series has been studied by Puschin⁹ who found that all alloys had the same potential as lead which he interpreted to mean that neither solid solutions nor compounds were formed. The electrical conductivity of the series has been

¹ Guertler, "Metallographie," Bornträger, 1912, Vol. 1, p. 792. Dessau, "Physikalische Eigenschaften der Legierungen," Vieweg, 1912, p. 87. Bornemann, "Die Binaren Metallegierungen," Knapp, 1909, p. 232. Reinglass, "Chemische Technologie der Legierungen," Spamer, 1919, p. 13. Desch, "Metallography," Longmans, 1922, p. 400. Tammann, "Lehrbuch der Metallographie," Voss, 1921, p. 220. Hoyt, "Metallography," McGraw-Hill B. ok Co. 1921, p. 52.

² Roland-Gosselin, Bull. soc. encour. ind. nat., [5] 1, 1301 (1896).

³ Ewen, J. Inst. Metals, 4, 135 (1910).

⁴ Stead, J. Soc. Chem. Ind., 16, 200 (1897).

⁵ Campbell, J. Franklin Inst., 154, 205 (1902).

⁶ Gontermann, Z. anorg. Chem., 55, 419 (1907).

⁷ Loebe, Metallurgie, 8, 7 (1911).

⁸ Leroux, Compt. rend., 156, 1764 (1913).

⁹ Puschin, Guertler, "Metallographie," Bornträger, 1921, Vol. II. p. 322.

investigated by Mathiessen¹⁰ who found a break in the curve at the composition corresponding to the formula PbSb. His figures near the lead end are too far apart to allow any conclusions to be drawn concerning the formation of solid solutions. The conductivity of liquid lead-antimony alloys has been investigated by P. Muller¹¹ and no evidence is found of a compound existing in the liquid state. The specific heat of the lead-antimony alloys has been determined by R. Durrer¹² who found that at constant temperature the specific heat was a linear function of the concentration, indicating no compound or solid solution formation. The hardness of lead-antimony alloys has been investigated by Saposhinkow and Kanewsky¹³ who concluded that neither compounds nor solid solutions were formed.

In a recent investigation Ludwick 14 finds that the hardness of annealed alloys varies smoothly with the antimony concentration up to 8%, the highest concentration investigated. However, when the 2% alloy is annealed it increases sharply in hardness, but no great change is produced in the others by this treatment. Ludwick does not offer any explanation of this but it would appear to indicate the formation of a solid solution up to about 2% of antimony. The most recent investigation of these alloys is that of Gurevich and Hromatko 15 who find the maximum tensile strength in an alloy containing 10% of antimony.

Our interest in the lead-antimony system was from the standpoint of the manufacture of cable sheath and we were, therefore, particularly concerned with alloys containing up to 2% of antimony. It is obvious that in an extrusion process the temperature of working must not be above the melting point of any of the constituents of the alloy but on the other hand it is advantageous to use as high a temperature as possible, as the plasticity of metals approximately doubles for every 10° rise of temperature. Accordingly, the maximum extrusion temperature for lead-antimony cable sheath depends on the equilibrium near the lead end of the system. The present investigation was, therefore, made with a view to determining the equilibrium in the low-antimony alloys; however, in the course of the investigation it was found desirable to extend it less completely to alloys containing about 13% of antimony.

Investigation

The Solidus Curve of Lead-Antimony Alloys.—The method adopted for the study of the low-antimony alloys was based on the differential heating curve. A small cylinder of pure lead was used as the neutral body which was connected with a similar cylinder of the alloy under test by a copper-constantan thermocouple. The differential e.m.f. was measured on a high sensitivity galvanometer so arranged that its sensitivity was about 70 mm. of scale per microvolt. The actual temperature for the furnace was determined by means of a copper-constantan thermocouple and a

¹⁰ Mathiessen, Z. anorg. Chem., 51, 415 (1860).

Muller, Metallurgie, 7, 730 (1910).
 Durrer, Physik. Z., 19, 86 (1918).

¹³ Saposhinkow and Kanewsky, J. Russ. Phys. Chem. Soc., 39, 901 (1909).

¹⁴ Ludwick, Z. anorg. Chem., 94, 161 (1916).

¹⁵ Gurevich and Hromatko, J. Chem. Met. Eng., 25, 62 (1921).

small potentiometer and was accurate to 0.5° . This apparatus, although laborious to operate, probably gave as accurate results as could have been obtained with a recording instrument. The rate of heating was such that a temperature of 300° was reached in about 2 hours. Some of the results of these experiments are shown in Fig. 1, corrected for the calibration of the thermocouple made at the melting points of pure tin and lead. The unannealed alloys show a eutectic arrest at 258° even when only 0.5% of antimony is present, but a few hours' annealing causes the disappearance of this arrest in alloys containing up to 2%. The 2% alloy becomes free from thermal evidence of the presence of the eutectic only after 200 hours' heating at 235° , and in the 3% alloy the eutectic still persists after this time. The evidence from these heating curves would then indicate that

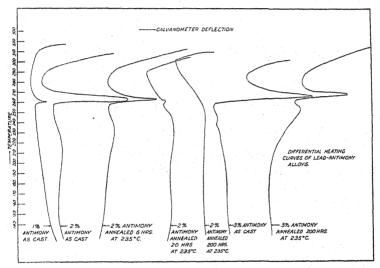


Fig. 1

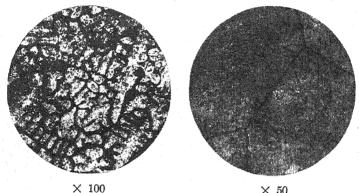
as much as 2 to 3% of antimony dissolves in lead when sufficient time is given. This slowness of attaining equilibrium is also characteristic of the lead-tin alloys as has been found by Rosenhain and Tucker.¹⁶

Microscopic Examination.—Microscopic examination confirms the findings of the thermal analysis in every respect. The eutectic which is present in the unannealed alloys disappears on annealing the alloys containing 2% of antimony or less. Fig. 2 shows micrographs of the 2% alloy before and after annealing. The etching is with silver nitrate and nitric acid. These microphotographs themselves would seem almost sufficient evidence for the formation of solid solutions in this system.

The Liquidus Curve of the Lead-Antimony Alloys and the Possibility of Compound Formation.—In order to have further data on the

¹⁶ Rosenhain and Tucker, Trans. Rov. Soc., 209, 89 (1908).

freezing-point curve of lead-antimony alloys to supplement those of Gontermann, for the purpose of drawing the complete equilibrium diagram, several determinations were made. The apparatus consisted of an electric crucible furnace in which was placed a crucible of alloy, the temperature of which was determined by means of a mercury thermometer calibrated in freezing lead and tin, and compared with the thermocouple used in



× 100 × 50

Fig. 2.—2% Lead-antimony alloy polished with MgO; etched with silver nitrate and nitric acid

Left, as cast

Right, annealed for 200 hours at 235°

the differential heating curves so that no discrepancies might arise in comparing the two results. The corrected results from these determinations and those from the previous heating curves are shown in the following table.

TABLE I
THERMAL ARRESTS IN LEAD-ANTIMONY ALLOYS

Composition % Sb	Cooling e	ANTIMONY ALLOYS urve H Solidus	Heating curve Solidus		
Pure lead	327.1				
0.5	326	none			
0.75		above	315		
1.0	321.5	none	309		
1.3			305		
1.8			300		
2	313	245	292		
3.0	305	245	258		
4.0	301	247			
10.4	255	247			
11.0			258		
12			258		
12.5		247			
13	252	245	253		
16	272	245			

There is a difference of several degrees between the positions of the solidus as determined by the cooling and heating curves, respectively.

The eutectic temperature from the cooling curves agrees well with that of Gontermann, namely, 245-246°, but the eutectic temperature on heating is

10° higher. In order to be certain of the reality of this hysteresis, both a heating and a cooling curve were obtained by use of the differential apparatus and a 3\% antimony alloy. The resulting curves are shown in Fig. 3 and leave no doubt as to the existence of the hysteresis. Our work has not been carried far enough to offer a complete explanation of this phenomenon. The equilibrium diagram shown in Fig. 4 shows our tentative interpretation of the results. The diagram assumes the formation of a compound Pb₄Sb containing 12.6% of antimony which forms an eutectic with its solid solution in lead at 10% antimony. The data are not sufficient to fix these points accurately, however. This compound, forms very slowly and when the mixture is cooled is not formed from the liquid but from the solid eutectic between antimony and solid solution. As a result of the reluctance of this compound to form,

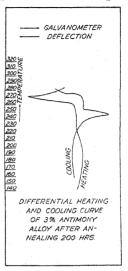
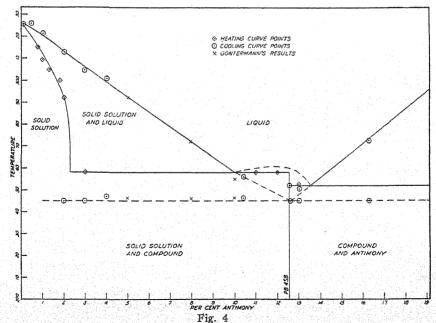


Fig. 3

the system as it cools behaves as if it were an antimony-solid-solution eutectic, and hence freezes at 247°. When this is heated the compound forms and the melting point is the eutectic point between compound and



solid solution at 258°. Mazzotto's explanation¹7 of a similar hysteresis in the lead-tin eutectic is that the eutectic supercools with relation to the separation of tin. A similar supercooling with relation to antimony does not seem to be the explanation of our results, since the freezing point is not raised by seeding.

My thanks are due to Mr. G. S. Rutherford in charge of the Chemical Division for his interest and cooperation in this work.

Summary

Investigation by means of differential heating curves and microscopic examination has shown that antimony is soluble in solid lead up to between 2% and 3% of antimony at the eutectic temperature.

The alloys containing up to 13% show a higher eutectic temperature on heating than on cooling. A suggestion for the interpretation of this is made and a tentative equilibrium diagram drawn.

This investigation is being carried further to determine the solubility curve for antimony in lead at temperatures below the eutectic and to obtain further data on the possible existence of a compound in the system.

CHICAGO, ILLINOIS

[Contribution from the Chemical Laboratory of Harvard University, and the Fixed Nitrogen Research Laboratory]

ANALYSIS OF HYDROGEN FOR TRACES OF NITROGEN¹

By R. L. Dodge Received May 7, 1923

The usual method for the determination of hydrogen in a mixture of gases by combustion over copper oxide has been modified and applied to the determination of traces of nitrogen in hydrogen. The details of the modified procedure are described in this paper. This procedure was employed in the analysis of hydrogen used for some special tests on ammonia catalysts. It is also useful for the analysis of hydrogen which is to be liquefied, since traces of nitrogen interfere materially with the liquefaction.²

Briefly, the method consists in burning large amounts (12–20 liters) of hydrogen over heated copper oxide in an evacuated system, circulating the residual gases over copper oxide to insure complete removal of the hydrogen, collecting the residual unburned gases (designated as nitrogen), and measuring them by the usual gas volumetric method. The volume

- ¹⁷ Mazzotto, Intern. Z. Metallog., 2, 269 (1911).
- ¹ The expenses of this investigation were in large part defrayed by the United States Fixed Nitrogen Research Laboratory,
- ² Dr. C. W. Kanolt of the Bureau of Standards, Washington, D. C., in connection with his study of the liquefaction of hydrogen, developed, subsequent to this work and independently of it, a similar procedure.

of hydrogen burned is calculated from the volume of water formed by the combustion.

Apparatus.—The apparatus is shown diagrammatically in Fig. 1.

The combustion tube A is of Pyrex glass, approximately 34 cm. long and 25 mm. in internal diameter, and contains about 350 g. of copper oxide.³ The heating is accomplished by means of the external resistance heater B. A Pyrex glass buret C, immersed in ice water, serves to collect the water formed by the combustion. Connection to the rest of the apparatus, which is of soft glass, is made through the ground glass joint (x, y). The bulb D (about 300 cc.) and stopcocks (d, e) make possible the circulation of the residual gases through the copper oxide to insure complete combustion of the hydrogen. The stopcock (c) controls the rate of admission of the hydrogen to the combustion system. The Töpler pump F serves to evacuate the combustion system. The McLeod gage J indicates the degree of evacuation. The gases removed by the Töpler pump are collected and measured in the water-jacketed buret G. H is a phosphorus pentoxide tube for the absorption of the traces of water uncondensed in the buret C.

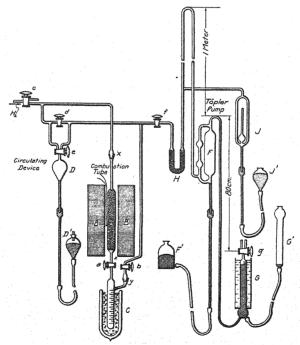


Fig. 1

'Procedure.—The hydrogen to be analyzed is dried and admitted through the Cock c to the combustion system, which has previously been evacuated to a pressure of 0.01 mm. of mercury.⁴ During the combustion,

³ A great excess of copper oxide is necessary, since reoxidation after an analysis is slow. The reoxidation is accomplished by heating the material to about 400° in a current of oxygen.

4 When both the initial and final evacuations are carried to the same point, errors due to incomplete evacuation are negligible.

Cocks d and f are closed. The rate of admission of the hydrogen is limited by the temperature of the combustion in the copper oxide tube, which should not exceed 400°, as above this temperature metallic copper forms a slag with Pyrex glass. Care must be taken to maintain a pressure in the hydrogen supply line greater than atmospheric to avoid inadvertent contamination of the hydrogen with air.

After a sufficient amount of hydrogen has been burned, as indicated by the water collected in the buret C, Cock c is closed and the gases remaining unburned in the combustion system are circulated through the copper oxide tube and buret by manipulation of the leveling bulb D' and the 3-way cock (e). Warming the combustion tube at z during the circulation insures transfer of all condensed water to the buret.

When continued circulation causes no further diminution in volume of the residual gas (indicated by using the bulb D as a rough McLeod gage) Cocks a and b are shut and d and f opened. The residual gas is then pumped into the water-jacketed buret G, where its volume is measured.

An error of 0.05 cc. in the volume of nitrogen causes an error of about 0.0005% in the percentage of nitrogen. An error of 0.01 cc. in the water formed causes an error of about one part in 200 in the actual percentage of nitrogen or, with a nitrogen content of 0.5%, an error of 0.002%.

The nitrogen lost by solution in the water formed during the combustion is, for an apparatus of this size, less than 0.04% of the total nitrogen.

The nitrogen left in the free space of the water buret is less than 1% of the nitrogen collected. This is within the limit of accuracy of the method for hydrogen containing less than 0.5% nitrogen. In using the method for hydrogen containing more than this amount of nitrogen, it is advisable to open the water buret to the combustion system for an instant after the first removal of the nitrogen and to collect this additional nitrogen by a second evacuation.

Results.—The method was standardized by analysis of "pure" hydrogen. This gas was generated in a modified form of Edwards' hydrogen generator⁵ from c. p. air-free sulfuric acid and c. p. mossy zinc. The generator was equipped with mercury-sealed stoppers and was evacuated before the acid was admitted. A 50% excess of zinc was used. The results of the analysis are given in Table I.

The analyses of "pure" hydrogen indicate that any errors due to liberation of incombustible gas by reduction of copper oxide or by solution of the zinc and the acid of the generator are less than 6 0.005%.

⁵ Edwards, J. Ind. Eng. Chem., 11, 961 (1919).

⁶ Auxiliary experiments show that the gas liberated by the copper oxide on solution in acid is less than 0.5 cc. for every 90 g. of CuO, this being the limit of accuracy of the determination. It is probable that the actual value is considerably below this. See Richards, *Proc. Am. Acad.*, 26, 276 (1890).

TABLE I

	KESULIS					
Gas analyzed		Observed volume H ₂ O Cc.	Vol. of H ₂ 0°, 760 mm. burned Liters	Obs. vol. "N ₂ "a 0°, 760 mm. Cc.	% "N2"	Av.
"Pure"	1	10.0	12.4	0.52	0.004	
	2	9.2	11.4	0.42	0.004	
						0.004
"Special"	1	11.4	14.2	6.51	$(0.046)^b$	
	2	11.4	14.2	5.78	.041	
	3	10.9	13.6	5.75	.042	
						.043
Ordinary	1,	11.0	13.7	64.28	.470	
	2	9.5	11.8	55.40	.470	
						.470

^a That is incombustible gas, unadsorbed by cuprous ammonium chloride or potassium hydroxide; it may contain argon and other inert gases.

^b The hydrogen supply line was under less than atmospheric pressure for a short time allowing possible contamination of the hydrogen with air.

"Special" hydrogen was taken from a commercial tank which had been filled as nearly as possible directly from electrolytic cells, special precautions being taken to remove all air from compressors, lines and tank before filling. It is probable that 0.04% represents the minimum percentage of inert constituents in commercial electrolytic hydrogen.

"Ordinary" hydrogen was taken from a commercial tank chosen at random.

In conclusion the author wishes to express his appreciation for the valuable assistance of Professor Arthur B. Lamb, under whose supervision this work was conducted.

Summary

A modification of the usual method for the determination of hydrogen by combustion over copper oxide has been devised and applied to the analysis of hydrogen for traces of nitrogen.

Large quantities of hydrogen (12–20 liters) were burned by circulation over heated copper oxide in a previously evacuated system and the hydrogen determined by measuring the water formed. The residual nitrogen was pumped off and measured.

The method is accurate to 0.005%.

CAMBRIDGE 38, MASSACHUSETTS AND WASHINGTON, D. C.

[Contribution from the Chemical Laboratories of Columbia University, No. 412]

THE DESIGN AND USE OF CONDUCTANCE CELLS FOR NON-AQUEOUS SOLUTIONS

By J. Livingston R. Morgan and Olive M. Lammert Received May 11, 1923

Introduction

In the course of an investigation involving the precise measurement with non-platinized electrodes of the electrical conductance of solutions in non-aqueous solvents, it has been found necessary to take certain precautions in the selection and use of the conductance cell. Since the difficulties necessitating such precautions are those which would be encountered by others attempting to determine the conductance of non-aqueous solutions within the range from 2×10^{-3} to 2×10^{-7} reciprocal ohms, with an accuracy of 0.1% or less, the experimental method followed is given in some detail.

Washburn¹ from the theory of the Wheatstone bridge, has derived equations relating for aqueous solutions the minimum allowable area of the cross section between the electrodes and the distance between them; Taylor and Acree² have taken up in some detail the difference in the results obtained using non-platinized electrodes with varying frequency and voltage, and have given an experimental criterion for good cells; Schlesinger and Reed³ have also emphasized this point; Haworth⁴ investigating the variation of the resistance with frequency, using a different type of Wheatstone bridge, has confirmed Taylor and Acree's results, as have also Kraus and Parker.⁵

It is the object of this paper to correlate the work of these previous investigators with the results of this research in the hope that the cell design and technique developed will give comparable results from all different investigators working with non-platinized electrodes.

Bridge Assembly.—The bridge assembly was made up of standard commercial instruments of the usual type now recommended for precision work; the source of current was a Vreeland oscillator operating at a frequency of either 500 or 1000; the roller-type of Wheatstone bridge was used, and 2 dial resistance boxes, the smaller 1, 10 and 100 dials, bifilar wound with an aggregate resistance of a thousand ohms, and the larger a 1000- and 10,000-dial box of the Curtis⁶ type; 2 variable air condensers were employed with a maximum capacity of 0.005 mfd. and 0.00125 mfd.,

- ¹ Washburn, This Journal, 38, 2431 (1916).
- ² Taylor and Acree, ibid., 38, 2403, 2415 (1916).
- ³ Schlesinger and Reed, ibid., 41, 1727 (1919).
- ⁴ Haworth, Trans. Faraday Soc., 16, 365 (1921).
- ⁵ Kraus and Parker, This Journal, 44, 2429 (1922).
- 6 Curtis and Grover, Bur. Standards Bull., 8, 3 (1911).

respectively. The telephone was a Baldwin head piece, Type F, with an impedance of 2000 ohms.

Both bridge and resistances were calibrated in the Ernest Kempton Adams Precision Laboratory using direct current and a D'Arsonval galvanometer; the resistances by direct comparison with resistances calibrated at the Reichsanstalt loaned by the Columbia University Department of Physics; the bridge by the Kohlrausch method.⁷

A water-bath regulated at $25^{\circ} \pm 0.002^{\circ}$ by the method of D. J. and J. J. Beaver* was used for most of the work. An oil-bath regulated in the same way was used for the higher resistances when necessary.

The usual grounding and shielding between different parts of the apparatus and of the leads was used. Furthermore, the Vreeland oscillator, which was in the same room but at some distance from the assembly, was shielded and the shield grounded in such a way that no stray currents could be heard in the telephone. The bridge was placed close to the baths with the leads of such length in either arm of the set-up that no lead correction was necessary, the leads being connected to the cells in the way recommended by Washburn.

Comparison Solutions.—The first difficulty encountered in this work was the lack of a suitable solution for comparing the cell constants, one with the other. In any work requiring more than one conductance cell, liquids for the purpose of comparing the relative constants of the cells are as necessary and important as the standard solution employed to find the absolute constant of any one of them. The customary method of simply diluting with water the liquid used for calibrating the cell was found to be unsatisfactory, for the solutions would have to be so dilute $(0.0002\,M)$ as to make it difficult to keep them free from contamination in handling as well as in measuring in glass cells.

The most convenient and satisfactory comparison solutions we have found are those obtained by diluting the calibrating solution of potassium chloride with 95% alcohol. Such a solution was forced into the cell by a pressure of purified air. The air, furnished by a water pump and purified by passage successively through solutions of sulfuric acid, potassium hydroxide, through water, and through soda lime, was then bubbled through some of the alcoholic solution of like concentration to give it the same pressure of vapor there as in the air above the solution. By filling the cell, in this way conductances of the same solution could be duplicated exactly throughout the entire range.

Variation of Resistance with Frequency.—Taylor and Acree have found with bare platinum electrodes (1) that the difference in the resistance

⁷ Kohlrausch and Holburn, "Leitvermögen der Elektrolyte," Leipzig, B. G. Teubner, 1898, p. 47.

⁸ Beaver and Beaver, J. Ind. Eng. Chem., 15, 359 (1923).

of a solution at frequencies of 1000 and 600 decreases as the diameter of the electrode increases, (2) that for a given electrode this difference decreases as the resistance of the solution increases from 11.492 to 534.4 ohms, (3) that the resistance of a cell decreases as the frequency is increased from 60 to 2000 cycles. To obtain then the "true electrical resistance" of the solution the authors suggested one of the following methods: (1) an extrapolation of the resistances to infinite frequency, which involves the measurement of each resistance at several frequencies; (2) the use of their extrapolation formula in terms of resistance, frequency and inductance, which necessitates the use of standard inductances or capacities; (3) an increase in the size of the electrode to at least 25 mm., preferably to 50 mm., at the same time with a construction of the cell and a method of using such that the resistance of the solutions measured in that cell is above a certain minimum.

The first two methods call for inconvenient experimental procedures and calculations; the third method possesses the advantage that any necessary alterations in the design of the cell or any restrictions, which must be placed on the resistance of the solutions measured in the cell, can be made once and for all at the beginning of the research. The subsequent determinations involve no more labor than when platinized electrodes can be used. Furthermore, if by simply fixing the minimum resistance to be measured in a given cell, small electrodes can be used, the

TABLE I

THE VARIATION OF THE APPARENT RESISTANCE WITH A CHANGE IN FREQUENCY USING CELLS WITH DIFFERENT AREA OF ELECTRODE SURFACE AND SOLUTIONS OF DIFFERENT ELECTROLYTES IN DIFFERENT SOLVENTS

Resista	ance R	Diff, in R at 1000 and 500 in %	Resista 1000~	nce R 500~	Diff. in R at 1000 and 500 in %
C	Cell 6—Brigi	IT ELECTRON	ез, 13 Мм. г	N DIAMETER	
		KCl-water	solutions		
274.22^{a}	277.14^a	1.055	8946.9	8954.5	0.085
584.02^{a}	588.05^a	0.690	9086.0	9093.5	.083
1455.05	1457.8	.189	10644.5	10653	.080
2264.0	2268.6	.203	13047	13059	.092
3419.4	3422.3	.085	13352	13365	.097
4909.6	4912.8	.065	18113	18138	.138
6309.4	6314.0	.073	26889	26938	.182
6640.6	6644.5	.059	30190	30250	.198
6853.3	6857.0	.054	39882	39992	.276
7260.8	7267.5	.092	42277	42397	.284
8529.0	8535.5	.076	65701	65971	.411
	K	Cl-alcohol-wa	ter solutions		
12095	12105	0.083	43490	43620	0.299
16680	16700	.120	82910	83305	.476
24515	24550	.143			
SCOPPEDUR PRODUCTION OF WA	STEPS AND THE SERVICE SERVICES		na walio Sala Talikitan		

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,	1020	C	ONDUCIAL	NCE CELLS		
		I,	iBr-acetop	henone solutio	ons	
	17270	17290	0.116	92100	92500	0.424
	32950	33010	.182	203496	205645	1.056
	C					
	CELL			•	. IN DIAMETER	2
	100 404		KCl-water			
	183.46^{a}	185.50^{a}	1.112	1255.8	1259.4	0.287
	360.68^{a}	363.10^a	0.671		9440.0	.074
	857.1	859.92^{a}	0.329	• • •	•••	• • •
				ater solutions		
	190.82^{a}	192.42^{a}	0.838	6783	6787.1	0.060
	440.35	441.47^a	.254	17388	17410	.127
	984.94	985.79	.086	23679	23725	.194
	2014.6	2016.0	.069	34954	35034	.229
	3617.3	3619.3	.055	38242	38340	.256
			r-acetophei	none solutions		
	2755.0	2758.0	0.109 $_{\odot}$	15595	15615	0.128
	14025	14040	.107	23111	23141	.130
	CELL	2-Roughen	ED ELECTE	RODES, 13 MM	. in Diameter	
			KCl-wate	r solutions		
	399.47"	404.55^{a}	1.522	2486.5	2492.0	0.221
	651.96"	656 .214	0.652	$2486.5 \\ 2516.0$	2521.0	.199
	914.77	917.74^{a}	,297	3531.2	3535.0	.108
	1114.2	1116.0	.162	9533.0	9540.0	.073
	1957.9	1962.9	.255			
		K	21-alcohol-v	water solutions	3	
	631.98	633.46^{u}	0.234		16599	0.084
	1391.3	1392.8	.108	18435	18460	.136
	2044.0	2046.0	.098	21018		.162
	3646 .3	3648.3	.055		29972	.174
	6945.0	6949.2	.060			
				none solutions		
	1440.7		0.090			0.122
	1440.7 2782.0	$1442.0 \\ 2785.0$		16395		.127
			.108	23550	23580	
	CELL	3—Rougher	VED ELECTI	RODES, 38 MM.	IN DIAMETER	
			KCl-water	solutions		
	112.23^{a}	112.23^a	0.000	973.1	973.1	0.000
		KC	l-alcohol-w	ater solutions		
	140.54^{a}	140.64"	0.071	701.23	701.23	0.000
	206.73	206.81^{a}	.039	1513.7	1513.7	.000
	369.22	369.29	.019	9054.6	9057	.027
		LiB	r-acetopher	none solutions		
	317.59	317.7^{a}	0.035	5637.2	5638.5	0.023
	1448.0	1448.0	.000	7466	7469	.040
	3076.1	3076.9	.036	12210	12213	.025
	1001	4007 0	000	00077	2025	000

^{4005.3 .030} ^a For this measurement a mica condenser was used.

4004.1

of a solution at frequencies of 1000 and 600 decreases as the diameter of the electrode increases, (2) that for a given electrode this difference decreases as the resistance of the solution increases from 11.492 to 534.4 ohms, (3) that the resistance of a cell decreases as the frequency is increased from 60 to 2000 cycles. To obtain then the "true electrical resistance" of the solution the authors suggested one of the following methods: (1) an extrapolation of the resistances to infinite frequency, which involves the measurement of each resistance at several frequencies; (2) the use of their extrapolation formula in terms of resistance, frequency and inductance, which necessitates the use of standard inductances or capacities; (3) an increase in the size of the electrode to at least 25 mm., preferably to 50 mm., at the same time with a construction of the cell and a method of using such that the resistance of the solutions measured in that cell is above a certain minimum.

The first two methods call for inconvenient experimental procedures and calculations; the third method possesses the advantage that any necessary alterations in the design of the cell or any restrictions, which must be placed on the resistance of the solutions measured in the cell, can be made once and for all at the beginning of the research. The subsequent determinations involve no more labor than when platinized electrodes can be used. Furthermore, if by simply fixing the minimum resistance to be measured in a given cell, small electrodes can be used, the

Table I

The Variation of the Apparent Resistance with a Change in Frequency Using Cells with Different Area of Electrode Surface and Solutions of Different Electrolytes in Different Solvents

Resist	ance R 500~	Diff. in R at 1000 and 500 in %	Resista	nce R 500~	Diff. in R at 1000 and 500 in %
(Cell 6—Brigi	IT ELECTROD	es, 13 Mm.	n Diameter	
		KCl-water	solutions		
274.22^a	277.14^{a}	1.055	8946.9	8954.5	0.085
584.02^a	588.05°	0.690	9086.0	9093.5	.083
1455.05	1457.8	.189	10644.5	10653	.080
2264.0	2268.6	.203	13047	13059	.092
3419.4	3422.3	.085	13352	13365	.097
4909.6	4912.8	.065	18113	18138	.138
6309.4	6314.0	.073	26889	26938	.182
6640.6	6644.5	.059	30190	30250	.198
6853.3	6857.0	.054	39882	39992	.276
7260.8	7267.5	.092	42277	42397	.284
8529.0	8535.5	.076	65701	65971	.411
	K	l-alcohol-wa	ter solutions		
12095	12105	0.083	43490	43620	0.299
16680	16700	.120	82910	83305	.476
24515	24550	.143			

	L	iBr-acetop	henone solutio	ons	
17270	17290	0.116	92100	92500	0.424
32950	33010	.182	203496	205645	1.056
CEL	l 4—Roughen	ved Elect	RODES, 13 MM	i. in Diameter	
		KCI-water	solutions		
183.46^{a}	185.50^{a}	1.112	1255.8	1259.4	0.287
360.68''	363.10^a	0.671	9433.0	9440.0	.074
857.1	859.92^{a}	0.329	• • •	• • •	• • •
	KC:	l-alcohol-w	ater solutions		
190.82^{a}	192.42^{a}	0.838	6783	6787.1	0.060
440.35	441.47^{a}	.254	17388	17410	.127
984.94	985.79	.086	23679	23725	.194
2014.6	2016.0	.069	34954	35034	.229
3617.3	3619.3	.055	38242	38340	.256
		-	none solutions		
2755.0	2758.0	0.109		15615	0.128
14025	14040	.107	23111	23141	.130
CEL	ь 2—Roughen	ed Electi	RODES, 13 MM	. IN DIAMETER	
		KCl-wate	er solutions		
399.47^{a}	404.55^{a}	1.522	2486.5	2492.0	0.221
651.96^a	656.21^{a}	0.652	2516.0	2521.0	. 199
914.77	917.74^{a}	.297	3531.2	3535.0	.108
1114.2	1116.0	.162	9533.0	9540.0	.073
1957.9	1962.9	.255			
			water solution		
631.98	633 .46"	0.234	16585	16599	0.084
1391.3	1392.8	.108	18435	18460	.136
2044.0	2046.0	.098	21018	21052	.162
3646.3	3648.3	.055	29919	29972	.174
6945.0	6949.2	.060		•••	•••
			none solutions		
1440.7	1442.0	0.090	16395	16415	0.122
2782.0	2785.0	.108	23550	23580	.127
CEI	л 3—Roughei			. IN DIAMETER	
		KCl-water			
112.23^{a}	112.23^a	0.000	973.1	973.1	0.000
	KC	l-alcohol-w	rater solutions		
140.54^{n}	140.64^a	0.071	701.23	701.23	0.000
206.73	206.81^a	.039	1513.7	1513.7	.000
369.22	369.29	.019	9054.6	9057	.027
		r-acetophe	none solutions	;	
317.59	317.7^{a}	0.035	5637.2	5638.5	0.023
1448.0	1448.0	.000	7466	7469	.040
3076.1	3076.9	.036	12210	12213	.025
4004.1	4005.3	.030	39355	39356	.002

economy of both platinum and solution possible would certainly justify any attempt to use such a method.

Therefore, since of all the cells on the market the Washburn Types A and B were the most carefully designed and capable of giving the range of conductance we needed with the minimum volume requirement and exposure of the solution to the air in transferring, an investigation was undertaken to determine for each cell a minimum resistance, above which the difference in the result due to frequency would be negligible. Taylor and Acree made no measurements above 534.4 ohms at 1000 cycles, but estimated that in general above 10,000 ohms the resistance measured at 1000 cycles would not differ from the true resistance by more than 0.01%. In Table I are values, each an average of a number of readings, for the resistance in ohms at 1000 and 500 cycles and the differences between these values, in percentage of the value of 1000 cycles. Cells 2, 4, and 6 are of Type B, Nos. 2 and 4 with a range at 10^{-4} to 10^{-6} reciprocal ohms, No. 6 with a range of 10^{-3} to 10^{-5} reciprocal ohms. Cell 3 is of Type A with a range of 10^{-6} to 10^{-7} reciprocal ohms.

While these data show that for Cells 2, 4 and 6 the differences in resistances at the two frequencies are comparable to the values obtained by Taylor and Acree, in the range covered by these investigators, for their 13 mm. bright electrodes, these differences do not decrease continuously in the manner predicted, but pass through a minimum between 5000 and 10,000 ohrus. That this phenomenon is not peculiar to any one cell or solution but to the size of the electrode is shown by the fact that when three different types of solutions are used in all 3 cells having the same size electrodes, the results are similar. That it is due to some cause inherent in the cell and not in the assembly is shown by the results obtained with Cell 3. In this case, with the larger electrodes, the differences are smaller throughout the entire range and do not increase above 10,000 ohms. The slight irregularities in these differences can readily be attributed to the difficulty in taking the readings at 500 cycles during the day, since the telephone was not tuned particularly to this frequency.

Apparently then, for cells having bare platinum electrodes, there is, for a maximum allowable error, no mimimum resistance above which a given cell may be used, but an optimum range of resistances throughout which the differences in resistance with differences in frequency may or may not, depending on the size of the electrode, be small enough to come within this limit of error. As the size of the electrode increases (at least up to 50 mm.) these differences in the resistances throughout this optimum range become smaller, and the range throughout which the cell may be used becomes larger. In other word, to choose the cell so that the resistance of a solution in it is large does not give the same results experimentally as to increase the size of the electrode and reconstruct the cell.

At very high resistances, 90,000 ohms or over, with Cell 3 in the waterbath, there was observed on some days a decrease in resistance at 500 cycles. When measured in an oil-bath this decrease disappeared and the usual slight increase was noted. At lower resistances, however, no differences in resistance of a cell in a water-bath or an oil-bath could be observed. Evidently this phenomenon is due to the capacity effects prevalent when a high resistance is measured in a water-bath. Since this effect was not always the same in the same laboratory and could conceivably be quite different in different laboratories, depending upon the grounding facilities, etc., Washburn's suggestion¹ that in the design of a conductivity cell a maximum resistance of 10⁴ ohms should be imposed when possible seems especially pertinent.

Throughout the work the capacities were measured and found to be greater at 500 than at 1000 cycles, but as the difference in the resistance at the two cycles increased the difference in the capacity decreased. Inasmuch as the condensers were of the type used to balance out capacity in the cell and were not standardized, the actual values are qualitative and are therefore not given.

Cell Design.—Since the only conditions imposed upon the use of Washburn's simplified Equation 4 in place of Equation 3 are that the

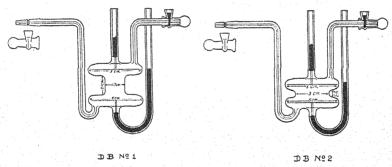


Fig. 1

specific conductance L^- shall not be less than 10^{-7} reciprocal ohms, the maximum resistance R not greater than 10^5 ohms, the frequencies not greater than 1000 cycles and the dielectric constant of the liquid not greater than 80, there was no reason why, for the non-aqueous solutions to be measured, the Type B cells could not be used, except for the fact that, due to the small size of the electrodes, the resistance at 1000 cycles is not the true resistance of the solutions. From Taylor and Acree's values and from the results with Cell 3 with electrodes 38 mm. in diameter, which showed that although there was a decided decrease in the difference at two frequencies this difference was not entirely eliminated, it was assumed that this error would probably be negligible were the diameter of the elec-

trodes increased to 50 mm. Accordingly, since the size of the electrodes was fixed, calculations were made by Washburn's Equations 24 and 25 to determine the dimensions of the construction between the electrodes.

The cells and their essential dimensions are shown in Fig. 1. The circular, sand-blasted electrodes were made of platinum 0.15 mm. thick with a rod 1.0–1.5 mm. in diameter securely welded to the center of the disc. The cells were of Jena glass. Since the solvents used were hygroscopic and volatile, the arms of the cells carried the mercury seals shown in the figure. Cell DB No. 1 has a cell constant approximately 1.39 and can be used for 0.02 N potassium chloride solution with a resistance of approximately 500 ohms. With 400–500 ohms minimum resistance there can be no errors due to the measurement at any one frequency, and only air condensers are needed. Cell DB No. 2 overlaps the range of Washburn's Type A cell and Cell DB No. 1, although the resistance does not fall below 500 or rise much above 10⁴ ohms. Unless extreme precision is desired, Washburn's Type A cell can be used with roughened or sand-blasted electrodes, although an increase in the diameter to 50 mm. would be an improvement.

Solutions having resistances ranging from 300 to 60,000 ohms were measured in both of the new cells. Since there was no difference in the resistance with the change in frequency to 500 cycles the resistance measured at 1000 cycles was assumed to be the true resistance of the solution.

The Methods of Cleansing and Drying Cells.-Little attention has been given by previous investigators to one factor which, in this Laboratory, has been found to be of the greatest importance, namely, the history and treatment of the electrodes previous to their use. Taylor and Acree² found that unless their cells were "scrupulously clean" the resistance of a filled cell varied with a change in voltage. This fact they used as a criterion of cleanliness, but suggested no method for either cleaning or drying. Possibly, since they used water solutions, they did not dry their cells before filling but rinsed them with successive portions of the solution to be measured. Such a procedure is almost impossible with hygroscopic solvents, however, and at best is wasteful of the liquids which are usually expensive and purified with difficulty. Kraus and Bishop¹⁰ also reported some trouble in checking their values for amyl alcohol when they used a cell that was dried after being steamed, but they gave no practical method for obviating the difficulty. In our own experience, when the cells were cleaned with chromic acid mixture, steamed, or rinsed with hot conductivity water, and then dried with warm, purified air either directly or after rinsing with redistilled alcohol, the values for the resistance of a given solution varied so capriciously and the variations were of such magnitude that quite

⁹ These cells were made by Mr. H. O. Morgan of Eimer and Amend.

¹⁰ Kraus and Bishop, This Journal, 44, 2206 (1922).

evidently the greatest source of error in the conductance method lies in the pre-treatment of non-platinized electrodes.

Since the discrepancy among results with any one solution was more apparent when the measurement was made in cells with electrodes near to one another, a series of determinations was made in which various methods of cleaning and drying Cells 3 and DB No. 2 were employed to discover if possible the cause of the error and, in any case, a method for the preparation of the cell that would give results consistent with those obtained when the cells were not dried but were rinsed with the solution. In the failure to develop such a method errors arising from the factors discussed in the foregoing sections of this paper are of little moment, as the error from this source alone frequently rises as high as 2 to 3%. The following is typical of the behavior of the 2 cells when the same solution is measured in both.

Cells cleaned with chromic acid-mixture, thoroughly rinsed with hot conductivity water and, without drying, finally rinsed with the solution to be measured, and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11799 ohms; Cell 3, 801 ohms.

Cells cleaned with chromic acid, rinsed as before, and dried by passing purified air through them; the same solution was used and the cells were allowed to stand for I hour after filling. Resistance: Cell DB No. 2, 11940 ohms; Cell 3, 816 ohms.

After cleaning, etc., the cells were allowed to stand for 24 hours. Resistance: Cell DB No. 2, 12158 ohms; Cell 3, 815 ohms.

The same cells were allowed to stand for an additional 12 hours. The resistance of the cells decreased because of movement of cell or lead but finally became constant. Resistance: Cell DB No. 2, 12112 ohms; Cell 3, 815 ohms.

The cells were refilled without cleaning or drying them. Resistance: Cell DB No. 2, 11805 ohms; Cell 3, 801 ohms.

The cells were cleaned with chromic acid mixture, rinsed and dried as before and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11860 ohms; Cell 3, 812 ohms.

The cells were refilled without cleaning or drying them $^{1}/_{2}$ hour after the previous measurement and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11780 ohms; Cell 3, 797 ohms.

The cells were refilled 1 hour after the previous measurement, and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11775 ohms; Cell 3, 799 ohms.

The same cells were again refilled, 2 hours after the previous measurement, and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11774 ohms; Cell 3, 799.55 ohms.

The cells were thoroughly washed with hot conductivity water. Treatment with cleaning mixture was omitted. Resistance: Cell DB No. 2, 11843 ohms; Cell 3, 803 ohms.

These results and others, of which these are typical, show that without a doubt the treatment of the cells with cleaning mixture was responsible for a considerable part of the error. Kohlrausch¹¹ has discussed the difficulty in measuring the conductance of solutions of acids and bases

¹¹ Ref. 7, p. 10.

with bare platinum electrodes due to the apparent absorption of the solute by the electrodes from stronger solutions, and the gradual liberation of the absorbed material to water and to the more dilute solutions. were this the only effect of the cleaning mixture in the case at hand the values for the resistances following such treatment should be lower, since the solution of material from the electrodes would increase the conductance of the solution between them. Furthermore, there should be no difference among values for wet or dry cells. Invariably in our work when a dry cell was used, the resistance of the solution was higher than the value in a wet cell, well rinsed. When the dried cell was immediately refilled without further cleaning or drying, the results were at first always too low, but on further refillings gradually rose to the normal value of the undried, rinsed cell. When the solution was left standing in the cell for 24 hours or more, the reading after the first refilling assumed its normal value. Were it not for the anomalously but uniformly high value obtained on the first filling of a dry cell, these data would seem to indicate the occurrence of phenomena similar to those observed by Kohlrausch.

The general theory underlying the measurement of an electrolytic cell by the Wheatstone bridge method is that when the cell, acting as a resistance and a capacity in series and shunted by a condenser in one arm, is balanced in the other arm by a pure resistance, shunted by an air condenser until no current flows through the telephone, the drop of potential along one half of the bridge is equal to the drop of potential along the other half, and therefore the resistances are equal. It is only, then, when there is a definite relationship between the resistances, the capacity and inductance, the drop of potential, and the current in one arm of the bridge to that in the other, that silence in the telephone can be obtained. A change in any one of these factors would cause a loss of balance in the bridge. In the present situation the only possible change is in the conductance cell itself, since the bridge assembly is identical for all the measurements.

In the cell the pure resistance is made up of the resistance of the solution and the small resistance of the electrodes both of which are constant for any one cell and solution. The capacity effects in a cell are assumed to be due to polarization and are dependent upon the area of the electrodes, the resistance of the solution between them and the frequency of the current. These also remain constant under the given conditions.

The only possibility remaining which would account for an unbalancing of the bridge network, otherwise in resonance, would seem to be that the cell filled with the solution in itself acts as a source of current. In this event the process of cleansing and drying the cells must in some way have so affected the electrodes that they are no longer similar pieces of the same metal dipping into the same solution but in effect two dissimilar electrodes

giving a potential difference across the terminals of the cell. In reality, then, we seem to be measuring, instead of a resistance and a capacity, a voltaic cell, the potential difference of which depends upon the difference in effect on the two electrodes of the pre-treatment, which in turn depends upon the difference in the specimens of platinum comprising each electrode and in the time and methods of pre-treatment.

If this is, indeed, the correct explanation of the abnormal behavior of the dried cells, the problem becomes one of finding how to bring the electrodes to the same potential after they are immersed in the liquid, and at the same time keep the resistance of the solution the same, or how to clean and dry the electrodes so that the potential difference of each in contact with the liquid is the same in the first place.

Accordingly, to determine whether it was possible to bring the electrodes to equilibrium after they had been treated with chromic acid and dried, the cell was filled and the electrodes short-circuited overnight, but no change in the measured resistance was observed. Without breaking the connection between the electrodes, the cell was cleaned with cleaning mixture, rinsed, steamed for several hours, rinsed with hot conductivity water and allowed to stand filled with water for several days. The cell was then rinsed with redistilled alcohol and dried. With the electrodes still connected the cell was filled with some of the same solution and allowed to come to temperature equilibrium in the bath. The short circuit was then removed, the lead wires put in place and the following readings taken. Resistance: Cell DB No. 2, 11785 ohms; Cell 3, 801 ohms.

The cells were then allowed to stand with the electrodes on open circuit, when the resistance began to rise. Resistance: Cell DB No. 2, 11795 ohms; Cell 3, 803 ohms.

The connecting wire was then again replaced and the filled cells allowed to remain in the bath overnight. The next morning the readings were the same. The cells were then refilled without drying or rinsing. Resistance: Cell DB No. 2, 11760 ohms; Cell 3, 799 ohms.

Of a number of such determinations made by cleaning and drying the electrodes, connected or unconnected, only those gave results approaching the normal value that were made after the electrodes had been connected throughout the entire process of cleansing, drying, filling, and attainment of temperature equilibrium. As this method seemed a possible solution to our problem, a systematic series of determinations was made on another solution to see what variations in the method were possible and how often the cell could be used by simply rinsing with alcohol and drying between refillings. In the interests of economy of space the results are summarized in the following statement.

The variations in the results are greater with Cell 3 than with Cell DB No. 2, and greater with Cell DB No. 2 than with Cell DB No. 1. In fact, no difference could be observed when Cell DB No. 1 was used even when the chromic acid cleansing was followed only by the thorough rinsing with conductivity water before drying, while with Cells DB Nos. 2 and 3 variations of the same order of magnitude as in the typical data given above were observed. When the electrodes were short-circuited during

the treatment with the cleaning mixture the discrepancies were reduced to about 1/4 of those observed when the cell was cleaned with the electrodes on open circuit; similar differences were noted when the cells were steamed, large errors being obtained if the cells were dried after steaming with the electrodes on open circuit. When the cells with the electrodes on open circuit were rinsed with hot conductivity water, without previous treatment with chromic acid mixture, the results with Cell DB No. 2 were usually normal but those with Cell No. 3 showed variations of 0.2-0.5%. It was only when the electrodes were short-circuited throughout the entire process of cleansing, drying and filling that consistent values for the resistance of a given solution were obtained in all cells. Furthermore, as soon as the short circuit was broken the resistance began to rise; when the connection was replaced the reading became constant. Evidently the electrodes prepared in this way are under some sort of a strain which is relieved by their taking up some of the solute from the solution when the current is broken. On refilling the cell after such adsorption has taken place without rinsing or drying, the next result is invariably too low, just as in the first experiments given in this section after the treatment on open circuit of the electrodes with cleaning mixture. This would seem to indicate that the adsorbed material was given back to the next solution. When the circuit was left open too long in taking a series of readings consistent results for the next refilling were not given by the usual procedure of short-circuiting, rinsing with alcohol and drying. In such a case, filling the cell with hot conductivity water and allowing the electrodes on open circuit to soak overnight seemed to relieve them of the adsorbed material and the cell could then be employed as usual with success.

The number of continuous determinations possible with only a thorough rinsing with alcohol and drying between refillings seemed to be contingent on the length of time the electrodes were left unshorted during measurement. When great care was taken in this respect the cells could be used all day for several weeks, particularly when they were soaked overnight in conductivity water and kept free from atmospheric contamination. With a cell of the pipet type, which does not permit much movement of the contained liquid, our criterion for the equipotentiality of the electrodes was the constant value obtained on moving the leads or the cell sufficiently to change the position of the solution between the electrodes. With cells of the bottle type, however, there is a constant mixing of all parts of the solution possible; whether the final result is burdened with an error can be determined only by a previous rigid examination of the cell with a known solution to determine what treatment is necessary to make the cell usable.

All in all, then, the term "clean" applied to conductance cells made up with bare electrodes takes on a new meaning, involving the attainment of electrodes which will act as similar pieces of the same metal toward a solu-

tion, and the maintenance of such a state of equipotentiality throughout the time required for the measurement of the resistance of the solution. The following procedure is recommended for the "cleansing" of the cells. The electrodes, during the entire operation, are connected by a heavy copper wire dipping into the mercury cups. The cell is then filled with hot cleaning mixture and allowed to stand for a few minutes, rinsed thoroughly with distilled water and finally filled with hot conductivity water: it is then steamed by allowing the steam to pass up through the water: this permits enough steam to condense so that in time the water that has been in contact with the electrodes is automatically siphoned off. The steaming is continued for several hours, after which the cell is filled with hot conductivity water and the outlets closed. After it has been allowed to stand overnight, the cell is rinsed with alcohol, dried with a current of warm purified air, and filled at once with the solution to be measured. Only when the actual readings are being taken must the short circuit be broken; it should be replaced between check readings. Whenever the cell is not in use it should be filled with hot conductivity water and tightly closed to keep the water as free as possible from contamination. This method has been found infallible with the 3 cells used; nevertheless, there seems still to be present an element of caprice, for some determinations made on another Washburn cell of the same type as Cell 3, and purchased at the same time, gave very unreliable results. In the first place, it was difficult to check the readings even when the cell was not dried; in the second place, extreme precaution was needed to obtain any sort of consistent results with dried cells; and in the third place, only a few refillings could be made before it was necessary to subject the cell again to a most rigorous cleansing process. With the possible variations in any one piece of a metal and the still greater possible variations in pieces from different sources it is to be expected that such differences among cells will be found. To Taylor and Acree's experimental criterion12 for good cells, namely, that whatever the solutions used, the ratios of the resistances of any solution in two such cells must be the same, must then be added the stipulation that such cells can be cleaned and dried successfully with comparative ease.

Especially interesting in this connection and confirmatory of our explanation of this phenomenon is the recent work of Willard and Fenwick¹³ and of Beans and Hammett.¹⁴ Willard and Fenwick found a great variation in the values for the potentials of supposedly similar platinum electrodes in a given solution, not only with different methods of pre-treatment but with repeated applications of the same method. Beans and Hammett found that a bare platinum electrode may differ in potential from a

¹² Ref. 2, p. 2403.

¹³ Willard and Fenwick, This Journal, 44, 2516 (1922).

¹⁴ Hammett, Dissertation, Columbia University, 1922.

similar platinized foil, both immersed in a $0.1\ N$ hydrochloric acid saturated with hydrogen, by as much as $0.3\ volt$. In both of these researches the treatments which gave the greatest deviations in the values of the potentials for similar electrodes were of the same variety as those that gave for us the greatest increase in the resistance of the solution. There remains the possibility that even for the most persistently unreliable cells a method using polarizing currents, on treatment with alkaline cleansing solutions such as alcoholic potash, or of saturating the electrodes with some gas other than air can be developed; an attempt to find such a method is now being made in this Laboratory.

Variation of Resistance with Voltage.—Kraus and Parker⁵ came to the conclusion that the only reason for the change in resistance with the change in voltage observed by them as well as by Taylor and Acree could not be the contamination of the solution from the cells, as suggested by Taylor and Acree, since with the greatest care they could not entirely eliminate this effect in some of their determinations. In the present research no change in resistance with the change in the impressed voltage has been observed when the electrodes were properly cleaned. With the great difference in the potential of the electrodes possible among different cells "cleansed" in the same or different ways, it is not surprising that such discrepancies should occur. In every case the method of cleansing and the criterion for clean cells should be given before any confidence can be placed in the experimental results.

Summary

A study has been made of the errors inherent in the design and use of conductance cells containing non-platinized electrodes, when employed for non-aqueous solutions, and the following general conclusions drawn.

- 1. In order to make accurate conductance measurements of dilute non-aqueous solutions, some comparison solution other than the very dilute aqueous solutions needed should be used, since the latter cannot be kept as free from contamination as the non-aqueous solutions which are to be measured. A solution of potassium chloride diluted with alcohol is suggested as the most convenient comparison solution.
- 2. The change in resistance with a change in frequency from 500 to 1000 cycles has been measured throughout a wide range of resistances, with a number of different cells and types of solutions. The results of Taylor and Acree have been confirmed in the range covered by them; however, the difference in resistance for small electrodes does not decrease continuously with an increase in resistance but passes through a minimum between 5000 and 10,000 ohms. There is not, as Taylor and Acree state, a minimum resistance above which a cell may be used with accuracy, but an optimum range which may or may not give results sufficiently accurate, depending upon the accuracy needed and the size of the electrodes;

as the size of the electrodes increases, the range and possible accuracy within the range increase. So choosing the cells that the resistance in them is large is not equivalent experimentally to increasing the size of the electrodes.

- 3. Cells have been designed, with the aid of Washburn's equations, which do not change in resistance with a change in frequency and which with the Washburn Type A Cell cover the range from 2×10^{-3} to 2×10^{-7} reciprocal ohms.
- 4. The method of cleansing and drying the electrodes has been found to be of far greater importance than any of the other factors involved, the errors from this source alone often being as high as 2 to 3%. The usual method of cleansing and drying seemed to make the cell, filled with its solution, not a resistance and a capacity but a voltaic cell, which gives the effect of an abnormally high resistance. A method is given for cleansing the cells which has for its underlying principle the production of 2 electrodes having as nearly as possible the same contact potential when immersed in the same solution; it involves thoroughly "scrubbing" the electrodes after any treatment with an acid cleaning mixture and keeping the electrodes short-circuited during all the processes of cleaning, drying and the bringing of the cell to temperature equilibrium.
- 5. It is believed that the difference in the potential developed by different electrodes when subjected to the same treatment accounts for the change in resistance with a change in the impressed voltage, and for the fact that some observers have not been able to eliminate the change by thorough cleansing while others have. The term "clean" applied to conductance cells should be more rigidly defined, if comparable values are to be obtained by different workers.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE OSMOTIC PRESSURES OF AQUEOUS SOLUTIONS OF PHENOL AT 30°

By Arthur Grollman and J. C. W. Frazer Received May 15, 1923

Introductory

The only reference to be found in the literature of an attempt to determine experimentally the osmotic pressure of phenol solutions is that of Naccari, whose results, being much lower than those theoretically expected and incapable of either duplication or accurate determination, were rejected by Naccari as unsatisfactory. Owing to the crudity of the method employed, which at its best could give but qualitative results, his data are of interest only from an historical standpoint.

¹ Naccari, Atti. accad. Lincei. 6, 32 (1897).

Indeed, even with the experimental refinements of the later methods as developed by Morse and Frazer, and their co-workers, only such compounds as the sugars were capable of accurate measurement. Failure to obtain results with substances of a low molecular weight were attributed to permeability of the cupric ferrocyanide membrane, or to the disintegration of the latter in the presence of such substances. Recent improvements in cell structure, which have been made in this Laboratory, have enabled the methods of direct osmotic-pressure measurements to be applied to a variety of substances hitherto considered beyond experimental determination, with an accuracy comparable to that of the best results obtained with cane sugar.

Phenol, presenting as it does rather anomalous behaviors in aqueous solution, was chosen for measurement, to determine whether the results so obtained could be correlated with its other properties. The great uncertainty existing regarding certain of its actions, such as cryoscopic behavior, hydration, etc., demanded an attack from another point of view in order to throw light on these subjects. The fact that it forms solutions with two coexisting phases was also suggestive. Moreover, all substances hitherto measured have approximated ideal solutions and obey the van't Hoff osmotic-pressure formula more or less closely. Phenol was, therefore, chosen, as it diverges widely from such behavior.

Experimental Part

The measurements were carried out throughout the solubility range at 30°, with nitrogen-filled manometers in a bath constant to 0.05°. The method was essentially that described and used by Frazer and Myrick² for sugar solutions, manometers being used, however, instead of the resistance gage there described. For low pressures, the manometric method is the most accurate though not the most convenient mode of measurement.

The solutions were analyzed with a Zeiss water-interferometer which permitted an accuracy exceeding that required by the manometric readings with a cathetometer.

The cells were perfected in a manner to be described in a later article;

TABLE I

			100 C 24 W	9		
Conen. of phenol per 1000 g. of H ₂ O Moles	O. p. obs. Atm.	Ratio: o. p. to conen.	(Concn. of phenol per 1000 g. of H ₂ O Moles	O. p. obs. Atm.	Ratio: o. p. to conen.
0.0986	1.42	1.45		0.2965	3.89	1.31
.1006	1.47	1.46		.3831	4.90	1.28
.1992	2.73	1.42		. 5214	6.67	1.28
.1999	2.83	1.42		.6672	8.42	1.26
.2716	3.73	1.37		.8936	11.20	1.25

² Frazer and Myrick, This Journal, 38, 1907 (1916).

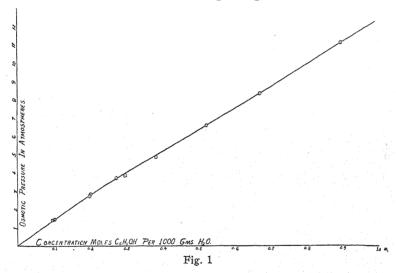
upon them were deposited the usual membrane of cupric ferrocyanide. These allowed but a slight permeability of the phenol, which was finally corrected for by analysis of the solutions. Equilibrium was obtained in less than 6 hours, even with the most concentrated solutions.

Table I and Fig. 1 give the results obtained. The curve is practically linear, tending to slope slightly towards the X axis with increasing concentration. The third and sixth columns show this tendency.

From the equation for ideal solutions,

$$P = \frac{RT}{V_0} \left(x + \frac{1}{2} x^2 + \frac{1}{3} x^3 + \dots \right)$$
 (1)

where P is the osmotic pressure, V_0 , the molecular volume of solvent and x, the molar fraction of solute, we can, neglecting the association of water,³



calculate the theoretical osmotic pressures of phenol solutions. This has been done in Cols. 2 and 6 of Table II. By interpolation of the observed values in Table I, the values for exact concentrations are obtained in Cols. 3 and 7.

Table II
Comparison of Theoretical with Experimental Results

Conen.	O. p. calc. from Formula I O. p. obs.	Calc. o. p. Obs. o. p. degree of assoc.	Conen.	O. p. calc. from Formula I		Obs. o. p. Obs. o. p. degree of assoc.
0.1	2.46 1.46	1.68	0.6	14.73	7.62	1.93
.2	4.92 2.84	1.73	.7	17.16	8.82	1.95
.3	7.38 3.93	1.88	.8	19.59	10.05	1.95
4	9.83 5.12	1.92	.9	22.02	11.28	1.95
.5	12.28 6.40	1.92				

³ Kendall, This Journal, 36, 1222, 1722 (1914); 37, 149 (1915); 38, 1309, 1712 (1916); 42, 2131 (1920).

A comparison of the observed values in Cols. 3 and 7 and the theoretical values calculated in Cols. 2 and 6 shows, as Cols. 4 and 8 indicate, that the former are approximately $^{1}/_{2}$ the latter, thus showing the probability of association of 2 molecules of phenol in aqueous solution to form a diphenolic complex.

If α is the degree of association of phenol, we must introduce this factor in Equation 1. Assuming the association to take place exclusively according to the equation, $2C_6H_5OH \longrightarrow (C_6H_5OH)_2$, instead of C, the molar concentration, we must use $\frac{\alpha c}{2} + (1-\alpha)c$ or $c\left(1-\frac{\alpha}{2}\right)$ and x, the molar

fraction, becomes
$$\frac{c\left(1-\frac{\alpha}{2}\right)}{55.5+c\left(1-\frac{\alpha}{2}\right)}$$

Making these substitutions in Equation 1 and substituting for the osmotic pressure, P, the observed values, we are able to calculate, α , the degree of association at the various concentrations. The decrease in the relative osmotic pressures with increasing concentrations is due to an increase in the degree of association of phenol with higher concentrations. The value of α increases from 86% for 0.1 M to 99% for 0.9 M solutions.

Beckmann and Maxim4 have derived values for the association of phenol in carbon tetrachloride and bromoform in various concentrations and at temperatures varying from the freezing points of the above-mentioned solvents to their boiling points under normal pressure. The degree of association is found to be most sensitive to dilution, rising for example from the value 1.21 for a solution of 0.599 g. of phenol in 100 g. of carbon tetrachloride at 54.1° to the value 1.58 when the same amount of solvent contains 2.738 g. The results in Table II, Cols. 4 and 8, derived from the osmotic pressure studies, lead us to the same conclusion, namely, that dilution is a potent factor in decreasing the association of phenol. This decrease of association with dilution may explain the great variance in the behavior of phenol in aqueous solutions on bromination. The formation of tribromophenol and tribromophenol bromide (tetrabromocyclohexadienone) may be due to the presence of both the simple molecule and the associated form in solution. Attention may be called to alternative explanations of the above phenomena, as due to the presence of a quinoid form, or as due to the presence of hydrobromic acid.

The Association of Phenol

The above conclusion that phenol exists in solution in an associated form is supported by its behavior in other respects, both physical and

⁴ Beckmann and Maxim, Z. physik. Chem., 89, 411 (1915).

⁵ Dinwiddie and Kastle, Am. Chem. J., 46, 502 (1911).

⁶ J. Chem. Soc., 121, 2810 (1922).

chemical. Essex⁷, from a study of the compressibility of phenol, applied the principle of Tammann⁸ whereby molecular magnitudes of anisotropic phases are determined, and finds that phenol exists as two forms of $(C_6H_5OH)_2$, a third species $-C_6H_5OH$ — being enriched at higher temperatures. Turner and English⁹ found, by a study of the freezing points in benzene, that the molecular weight of phenol varies from 149.6 to 194.5; these results are in the same order of magnitude as those derived from the osmotic-pressure measurements. Walden, ¹⁰ by a study of the specific cohesion, reaches the same conclusion. The surface-tension measurements of phenol solutions, ¹¹ cryoscopic measurements, etc., all point to association of phenol.

In its chemical reactions, also, phenol shows a tendency towards reacting not as a simple molecule but rather in an associated form. Thus the following compounds have been isolated: $2C_6H_5OH.H_2O;^{12}$ $2C_6H_5OH.TeCl_4;^{13}$ a series of compounds having the structure $2C_6H_5OH.Ca(OH)_2 \times H_2O;^{14}$ ($C_6H_5OH)_2H_2SO_4;^{15}$ as well as numerous other addition products. In all of these compounds 2 molecules of phenol react, which points to the probability that phenol reacts as the dimolecular compound $-(C_6H_5OH)_2$, as indicated by the values of the osmotic pressures.

Effect of Temperature on the Degree of Association

Solution of phenol is accompanied by a large absorption of heat. The measurements of various properties, such as ebullioscopic, etc., all give results indicating a decrease in the degree of association with increasing temperature. Applying the Le Chatelier principle, it is obvious that the compound formation must be exothermic and, vice versa, the dissociation of the double molecule takes place with an absorption of heat. We must, therefore, attribute the negative heat effect resulting on dissolving phenol as due to the breaking down of the more complicated structure with the formation of a certain percentage of simple molecules. The pure substance, therefore, exists practically entirely in an associated form; experimental studies of the molten material corroborate this (as, for example, Essex's work quoted above).

- ⁷ Essex, Z. anorg. Chem., 88, 189 (1914).
- ⁸ Tammann, Z. physik. Chem., 84, 293 (1913).
- 9 Turner and English, Proc. Roy. Soc., 105, 1786 (1914).
- ¹⁰ Walden, Z. physik. Chem., 65, 189, 266 (1908).
- ¹¹ Morgan and Egloff, This Journal, 38, 844 (1916). Feustel, Ann. Physik, [4] 16, 61 (1905).
- ¹² Smits and Maarse, Proc. acad. Sci. Amsterdam, 14, 192 (1911). Rhodes and Markley, J. Phys. Chem., 25, 527 (1921).
 - 13 Ber., 30, 2832 (1898).
 - 14 J. Russ. Phys. Chem. Soc., 45, 1535 (1914); Chem. Centr., 1914, I, 110.
 - 15 THIS TOURNAL, 36, 2507; ibid., 1222 (1914).

Summary

- 1. The osmotic pressures of phenol solutions have been determined throughout the solubility range at 30.0°.
- 2. From the results so obtained the degree of association of phenol in aqueous solution has been calculated, and it is found that the percentage of simple molecules existing in the dimolecular form varies from 86% for 0.1~M solution to 99% for 0.9~M solution. The pure material is entirely associated.
- 3. It is suggested that the variance in the chemical compounds formed on direct bromination of aqueous phenol solutions of varying concentration is attributable to the different molecular combinations present.
- 4. The great absorption of heat attending the solution of phenol is due to the partial decomposition of higher molecular forms, the reaction $(C_6H_5OH)_2 \longrightarrow 2C_6H_5OH$, being endothermic.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

IMPROVEMENTS IN THE MODE OF MEASUREMENT OF OSMOTIC PRESSURE

By Arthur Grollman and J. C. W. Frazer Received May 15, 1923

Introduction

Of the various experimental physicochemical methods, none is of greater importance than the measurement of osmotic pressure. The thermodynamic considerations of solutions are based on the concept of an osmotic pressure and all other properties of solutions are derivable from osmotic-pressure data. Of paramount importance is the fact that osmotic-pressure measurements are capable of the greatest refinement, being measurable with an extreme accuracy. Though we possess other accurate means of measurement such as of the freezing point and the vapor pressure, these are very limited, the former being confined to one temperature, the latter applicable over only a limited range of temperature. Osmotic-pressure measurements, on the other hand, can be carried out with equal precision over the range of temperature in which the solvent in question exists in the liquid form and throughout all possible concentration limits.

Despite these desirable conditions and advantages, measurements of osmotic pressures have been limited to a few substances, such as sugar and glucose. Substances of lower atomic weight, and especially electrolytes, have defied measurement and it has usually been assumed in the case of electrolytes that measurement is impossible because of the destructive effect on the semipermeable membrane and the permeability of the latter to such substances. The object of this investigation was so

to modify the present mode of measurement as to make it more widely applicable and, if possible, to apply it to the measurement of electrolytes.

The Cells and Membranes

Of primary importance in the experimental determination of osmotic pressure is the character of the clay cell used as the support of the semi-permeable membrane. Indeed, the lack of cells of proper texture was the cause of failure by early investigators. The cells used by Morse and Frazer in their work were made with every precaution to obtain a final product having a uniform porosity, a fine structure, and lacking, above all, any "air blisters." Such cells were obtained in the laboratory by carefully elutriating and washing the clays, pressing the obtained mixture, and finally turning to the required form on the lathe, after which the cell was baked and its collar glazed. The microscopic structure of such a cell (Type A) showed that it had a fine and uniform texture.

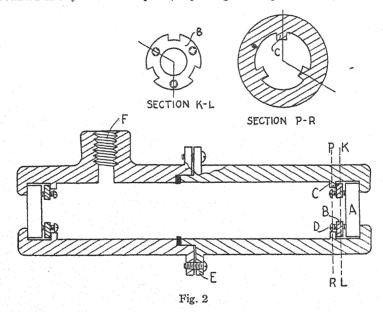
Since the function of the cell in measurements of osmotic pressure is to secure a support for the membrane to be used, it is perfectly obvious that the fineness of texture of the latter will depend entirely on the size of the pores of the cell itself. If there should happen to be a point where the cell wall is highly porous, the membrane, if deposited at all over this area, must necessarily be held but loosely, and the exertion of any pressure at this point would easily disrupt it.

The failure of early attempts to measure the osmotic pressure of solutions of electrolytes was usually attributed to the destructive effect of the electrolytes on the colloidal nature of the copper ferrocyanide membrane. To be sure, this is an important factor in such determinations, but it appeared likely that the failure of early attempts was due also, in a large measure, to the character of the cell itself. The fact that only substances of high molecular weight could be studied while other materials of molecular weights of a lower magnitude including electrolytes, passed through the semipermeable membrane suggested that cells of a finer structure might support membranes of a finer structure which, though incapable of prolonged existence in the presence of disrupting agencies would, nevertheless, prevent leakage of the solute and thus serve as true semipermeable materials for the period of time required to make a measurement.

To obtain cells with a texture finer than the one described above by the same method is scarcely possible. This cell was subjected during preparation to a pressure of about 3000 kg. per sq. cm. of surface of clay for 15 hours. Moreover, as shown later, cells of any appreciable thickness of finer texture than shown by Type A, although capable of supporting a membrane impervious to the solute would, nevertheless, fail to give accurate osmotic-pressure measurements. It was decided, there-

fore, to produce in the cells heretofore used some insoluble material which would give a support for the membrane. Microphotographs of cross sections of cells so prepared (Types B, C, D and E) showed darker areas representing the areas where the interior of the cell had been modified by the introduction of these fillings, whose extremely fine structure was indicated by the opacity to light which these sections showed under the microscope.

The Type B cell was filled with magnesium silicate by electrical diffusion. The cell to be treated was placed in an apparatus similar to that used in depositing the membrane, and a current (taken directly from the lighting circuit) passed between a roll of platinum foil placed within the cell, which served as the anode, and a foil (2 cm. wide) which surrounds the cell, dilute solutions of magnesium nitrate and sodium silicate serving as anolyte and catholyte, respectively. In this manner the required filling can be obtained in any thickness required, depending on the period of deposition. The



optimum results are obtained with an electrolysis of about 10 hours. The initial amperage, which varies with the porosity of the cell in question, ranged from 0.5 to 1 ampere under the above conditions and drops in 10 hours to 0.02–0.2 amperes. It was found that cells filled in this manner scarcely cracked on baking and gave most efficient results. After all treatments, the cells are baked in a pottery kiln for several days at $1000-1450^{\circ}$ and then, after thorough electrolysis with a 0.05% lithium sulfate solution to remove all air from the cell by endosmosis, the cell is electrolyzed with pure water until all electrolytes have been removed. It is then ready for the deposition of the membrane.

Type C cell was filled in a similar manner, except that sodium hydroxide was used instead of the silicate and the magnesium hydroxide thus formed was burned in the kiln. The filling was rather narrow and not at the very surface of the cell, but toward the interior.

Type D was filled exactly as was Type E cell but was not baked after filling. This was made evident in the photographs by the greater porosity of the baked cell due to the

contracting effect of heat on the filling. The baked cells invariably gave better results, which may be explained by the fact that too dense or too thick a filling does not allow free and easy diffusion of solvent through the cell which, in turn, results in a slow and incomplete attainment of equilibrium, despite the fact that with such cells no leakage or a negligible amount occurs.

Type E cell contained a filling of magnesium silicate produced as follows. The cell was placed in a solution of concentrated magnesium chloride which diffused and thoroughly filled the pores of the cell. After the outer surface had been washed, the cell was transferred to a solution of sodium hydroxide which on diffusion precipitated magnesium hydroxide in the cell. In order to produce a more insoluble filling, this was converted to the silicate by boiling in a 10% solution of sodium silicate. The above process was repeated several times until no more "filling" could be inserted. The "filling" was precipitated at the outer surface of the cell where it was desired, since it is here that the membrane is deposited. The main objection to this method of cell treatment is the fact that the majority of cells so treated crack on drying.

Type F cell was filled by diffusion. A cell filled with magnesium chloride and inserted in a beaker of sodium hydroxide was allowed to stand for several weeks. In this way a fine layer of magnesium hydroxide was precipitated where the solutions met, which was then converted to the silicate. One cell of this type was actually used in quantitative measurements and gave excellent results until finally it cracked from the pressure developed in use.

Deposition of Membrane.—It was found that the optimum and quickest results are obtained if, instead of bringing about the first deposition of the membrane by means of electrolysis as is commonly done, a modified form of the method described by Pfeffer¹ be used.

The cell is filled with a molar solution of cupric sulfate and placed in a beaker of water until the solute has diffused through the cell. The cell is then washed, the water is replaced with a molar solution of potassium ferrocyanide, and the arrangement allowed to stand overnight. Such a cell set up immediately with a $2\,M$ solution of sugar often gives the theoretical pressure which in the case of unfilled cells can only be obtained after from 6 months to a year of constant seasoning.

Discussion of the Cells.—The results already obtained by the use of filled cells in the case of phenol solutions² and qualitative measurements made, show that the above method of cell treatment accomplishes its purpose. Regardless of the magnitude of the molecular species under consideration, the leakage in any case is but minimal. However, it cannot be too strongly emphasized that non-leakage is not to be taken as a criterion of a successful measurement, as has been done by some investigators. The only criteria for a good measurement are the attainment of a pressure which remains constant for some time, non-leakage of solute and, above all, the ability to duplicate all results with other cells and measuring apparatus, in so far as the limit of accuracy of the method permits. Data based on measurements not fulfilling these requirements are to be considered worthless.

¹ Pfeffer, "Osmotische Untersuchungen," 1877.

² Grollman and Frazer, This Journal, 45, 1705 (1923).

Another point of superiority of the filled cells is the speed with which they attain equilibrium, which far exceeds the time required with unfilled cells. Indeed, measurements of 50 atmospheres' pressure have been attained with sugar solutions, using air manometers, within 20 minutes after setting up, and the fact that in such measurements a considerable diffusion of solvent must take place to produce the pressure, shows the potency of the force with which we are dealing.

A New Interferometer Cell for Use as a Pressure Gage

Besides the question of cells, whose improvement has been discussed above, the mode of measuring the pressure exerted is of fundamental impor-Nitrogen-filled manometers which have been used in the past have the great disadvantage that the time for equilibrium is rather long, since for its attainment, considerable solvent must pass through the cell. With electrolytes it is essential to make rapid determinations, since long contact with the solutions has a detrimental effect on the membranes. Hence, a more rapidly registering pressure gage was desired. Van Doren, Parker and Lotz³ have devised a method of measurement in which the change of refractive index with pressure as measured by the Zeiss waterinterferometer serves as a pressure gage. By the use of this instrument rapid determinations can be made. As developed by these investigators the instrument has, however, several defects. It is rather difficult to assemble, leakage at the glass windows being especially hard to avoid. Moreover, due to the manner in which the windows are held in place, the length of the pressure chamber is necessarily made small, which means a corresponding diminution in the sensitivity of the instrument, the sensitivity being directly proportional to the length of the column of liquid compressed.

The two objections mentioned above have been satisfactorily overcome by the modified instrument shown in Fig 1. This new form combines ease of assemblage and high sensitivity, the latter being twice that of the original instrument. As it is generally applicable wherever pressure measurements are to be quickly and accurately made, it will be briefly described.

It consists essentially of a brass tube, with optical glass windows inserted at its ends, which is held in place by means of a square block of brass through which are drilled 2 holes. One of these serves to hold the pressure chamber in place, while the other, which is contiguous to the first, holds the other window which, dipping into the water-bath of the interferometer, serves as the non-pressure or comparison chamber. By this arrangement only the pressure tube requires especial care in construction to avoid leakage, and it is this simplification which gives the instrument both ease in assemblage and greater accuracy. A plate screwed on the end blocks serves as a support of the chambers in the bath. Since the parts on being assembled assume the same relative position, no diffi-

³ Van Doren, Parker and Lotz, This Journal, 43, 2497 (1921).

culty is experienced by a change in the zero reading of the instrument such as would occur were the arrangement not exactly reproducible.

In order to introduce the glass windows into the ends of the pressure chambers from the inside, thus giving a tighter joint between glass and metal with increasing pressure. the pressure tube must be made in two parts. These are joined by the flange arrangement E, leakage being prevented by insertion of a washer made of steam packing where the two ends meet within the tube. Such washers do not flow under pressure as ordinary rubber does. The tube, which is otherwise of uniform bore throughout its length, has 3 points of projection, C, which serve to support the washer B. The glass windows, A, are circular, but have 3 notches corresponding to the 3 projections from the tube, in order that the windows may be slipped past these projections. After the windows are introduced as shown in the figure, a circular brass washer, B, having notches similar to those of the glass plate, is slipped beyond the projections, turned so that it is now supported by the projections, C, and the glass windows are held tightly against their supports by means of the screws, D. The windows are made air-tight by the use of a rubber solution which, after assemblage, is vulcanized by slow heating. The tube is joined by F to a mercury trap which in turn is connected to the pressure cell or to the source of the pressure to be measured.

The instrument as described above has a range of 30 atmospheres. This can be increased as described by Van Doren, Parker and Lotz³ by the use of thin glass plates inserted in the path of the beam passing through the non-pressure side.

Since the range of 30 atmospheres corresponds to 3000 divisions on the interferometer and since readings on the latter are capable of duplication within 10 divisions, the pressure readings are accurate to 0.1 of an atmosphere. The accuracy can be further increased by using a more compressible liquid than water in the instrument and interferometer bath and by the use of a longer pressure chamber and wider windows. The length of the pressure chamber of the instrument as described above was 80 mm. By arranging the mirrors and prisms of the interferometer so that there is a greater distance between the two beams, larger windows can be used in the pressure gage, which insures more accurate readings.

For a complete description of the use of the interferometer, the reader is referred to the papers⁴ by Adams, Cohen and Bruins, Löwe, and Haber and Löwe.

Owing to the difficulties inherent in most methods of pressure measurements, their limited applicability and accuracy, the use of the water interferometer should prove itself a most desirable substitute for certain methods heretofore employed.

Conclusion

It is hoped that with the modifications above described, the road is paved for the measurement of the osmotic pressure of electrolytes and other substances whose behavior in solution, as shown by the osmotic pressures

⁴ Adams, This Journal, 37, 1181 (1915). Cohen and Bruins, Z. physik. Chem., 103, 337 (1923). Löwe, Chem.-Ztg., 51, 405 (1921). Haber and Löwe, Z. angew. Chem., 23, 1393 (1910).

which they exert, may throw light on the important questions of solutions. Qualitative results obtained with lithium chloride, sodium nitrate, sodium acetate, cupric chloride, sodium chloride, ethyl alcohol and acetic acid are promising and though no successful quantitative results with concentrated solutions have as yet been obtained, experiments on the more dilute solutions are now in progress, the results with phenol having already been published.

Summary

- 1. The method of experimentally determining osmotic pressures has been improved by filling with various silicates the cells on which the membrane is precipitated.
- 2. Such cells are efficient supporters of the membrane, allow but a minimal leakage, a rapid attainment of equilibrium, and do not require long seasoning.
- 3. An interferometer cell has been devised which is capable of acting as an accurate and rapid pressure gage.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMHERST COLLEGE]

ELECTROMOTIVE-FORCE MEASUREMENTS WITH A SATURATED POTASSIUM CHLORIDE BRIDGE OR WITH CONCENTRATION CELLS WITH A LIQUID JUNCTION

By George Scatchard Received May 17, 1923

The determination of the activities of individual ion species is a very interesting and important problem of physical chemistry. The measurement of hydrogen-ion activity, often under the name of hydrogen-ion concentration or $P_{\rm H}$, is being applied to so many varied problems that a consideration of all the possible evidence as to the validity of the procedure becomes important. The applications themselves present a considerable body of evidence.

The electromotive force of a cell of the type, Pt, H_2 [HCl, AgCl Ag, can be derived rigorously from thermodynamics alone. At constant temperature and pressure it is $E_1 = E'_1 - RT/F \ln(a_{\rm H} \times a_{\rm Cl})$, where E'_1 is the corresponding electromotive force when the activities are unity, and the other symbols have their usual significance. This electromotive force is divided between the two electrodes; we will assume that it is so divided that the electromotive force at the hydrogen electrode is $E_2 = E'_2 - RT/F \ln a_{\rm H}$ and that at the silver-silver chloride electrode is $E_3 = E'_3 - RT/F \ln a_{\rm Cl}$. Although this generally accepted assumption is apparently incapable of direct proof there seems little reason to question it, for it is difficult to imagine a mechanism of the reaction in which the chloride ion

could affect the electromotive force of the hydrogen electrode except by changing the activity of the hydrogen ion. Without such an assumption any attempt to determine the activity of individual ions by electromotive-force measurements is hopeless.

The customary procedure for measuring the activity of a single ionic species is to use a single electrode in combination with a saturated potassium chloride bridge and a standard electrode, which involves the assumption that the potential drop is zero at the liquid junction: saturated potassium chloride, unknown. Then, since the electromotive forces at the standard electrode and at the junction of the electrode solution with the bridge are constant and may be included in E', the electromotive force of the whole cell is given by E_2 or E_3 . Corran and Lewis¹ have presented what they consider to be a proof of this equation for the hydrogen electrode in solutions of hydrochloric acid and sucrose in water. However, their proof contains the assumption that the electromotive force of the silver-silver chloride electrode is given by the equation, $E_4 = E'_4 RT/F \ln \sqrt{a_H \times a_{Cl}}$, which differs from E_3 . Since the value of E_3 follows necessarily from those of E_1 and E_2 , the result proved is incompatible with the assumption made to prove it, and the proof is invalid.²

The assumption that a saturated potassium chloride bridge eliminates liquid-junction potentials is usually based on the extension to solutions in general of the proof of Fales and Vosburgh⁸ for solutions of N and 0.1 N hydrochloric acid. The argument of Fales and Vosburgh depends upon the proof that the electromotive force at the liquid junction with saturated potassium chloride is the same for 0.1 N as for N acid, and that the most reasonable explanation is that both are zero. The authors recognize that this proof depends upon the assumption that "the combinations represented by Hg-HgCl x MHCl - x MHCl-H2 (1 atmos.) Pt change their pole potential differences by the same amount, but in an opposite direction, as we vary x."4 However, this assumption is not substantiated by the consistency of their results, for there are too many arbitrary variables. It is equivalent to assuming that the hydrogen and calomel electrodes each measure the mean activity of hydrogen and chloride ions, or that the ratios of the activities of the two ions are equal in these two solutions. The extension to all concentrations would require that the activities themselves be equal.

It seems more reasonable to make the assumptions of MacInnes:⁵ that (a) the activity of the chloride ion is the same in solutions of all uni-

¹ Corran and Lewis, This Journal, 44, 1673 (1922).

² H. S. Harned [*ibid.*, 42, 1808 (1920)] makes the same two contradictory assumptions, but uses them in only a few of his calculations.

³ Fales and Vosburgh, *ibid.*, 40, 1291 (1918).

⁴ Ref. 3, p. 1299.

⁵ D. A. MacInnes, ibid., 41, 1086 (1919).

valent chlorides at the same molality, and (b) equal to the activity of potassium ion in potassium chloride solutions. With these assumptions the difference between the 2 liquid-junction potentials is 6.4 mv.; both cannot be zero and there is no reason to suppose that either is.

From other results of Fales and Vosburgh it is possible to determine the electromotive force of the cell, Hg | HgCl, KCl (c_1) | KCl (sat.) | HCl (c_1), HgCl | Hg. A combination of Experiments 9, 18 and 23 gives 0.1 mv. when the solutions are 0.1 N. Expt. 1 give 8.3 mv. for 1 N solutions; corrected to equal molalities this becomes 8.9 mv. for 1.023 M solutions. By the MacInnes assumption (a), the electrode potentials cancel. The liquid-junction potentials between the solutions of potassium chloride are probably only a few tenths of a millivolt; the Nernst-Planck formula gives 0.6 and 0.4 mv. With this assumption the liquid-junction potential is small with 0.1 N solutions, but becomes large for N solutions.

A test of this assumption would be very simple by comparing the activity determined with a saturated potassium chloride bridge with that from cells without transport, but apparently the necessary measurements have never been made. The most direct comparison possible is one between the measurements of Fales and Morrell⁶ with the bridge at 35° and the values given by Lewis and Randall⁷ for cells without transport at 25°. The activities change with the temperature, but the general nature of the curves should be the same. Table I contains this comparison for the activity coefficients (activity divided by molality), and also for the activity coefficient of the hydrogen ion calculated by the MacInnes assumptions.

Table I

Comparison of Activity Coefficients in Hydrochloric Acid

Molality	$\sqrt{a_{\rm H} \times a_{\rm Cl}/m}$	$a_{ m H}/m$ Fales and Morrell	$a_{\rm H}/m$ MacInnes assumptions
0.0010	(1.00)	(1.00)	(1,00)
0.0100	0.94	0.94	0.94
0.1001	0.83	0.84	0.84
0.3017	0.78	0.84	0.83
0.6071	0.78	0.82	0.90
0.9161	0.82	0.82	1.02
1.229	(0.88)	0.87	(1.22)

The necessary change from moles per liter to molality is made by means of the density determinations of Fales and Morrell. Since their values are only relative, all coefficients are given on such a scale that the coefficient is unity for the $0.001\,M$ solution. It is apparent that the cell with saturated potassium chloride bridge measures neither the mean activity nor that of the hydrogen ion calculated by the MacInnes assumptions. For solutions $0.1\,M$, or more dilute, the agreement with the MacInnes assumptions is

⁶ Fales and Morrell, This Journal, 44, 2071 (1922).

⁷ Lewis and Randall, *ibid.*, **43**, 1112 (1921).

good, confirming our conclusions that the liquid-junction potential is very small with these solutions.

Hitchcock⁸ has used a saturated potassium chloride bridge with both hydrogen and silver-silver chloride electrodes in hydrochloric acid through the concentration range 0.001– $0.1\ M$, but his measurements were reproducible only to about 1 millivolt. His results show that the liquid-junction potential may be ignored within this range and within his experimental error.

Most applications of the saturated potassium chloride bridge involve the presence of a second solute. Some insight into the validity of assuming that the liquid-junction potential is eliminated in such cases may be obtained from the measurements of Corran and Lewis¹ on sucrose solutions if we recognize that the silver-silver chloride electrode measures the activity of the chloride ion and not the mean activity. These solutions have a particular interest in themselves on account of the importance of sucrose inversion to the study of reaction speed. The measurements on potassium chloride are made with a concentration cell with transport; those on hydrochloric acid with a saturated potassium chloride bridge.

Although a concentration cell with transport cannot be reversible on account of diffusion, it seems generally accepted that the derivation of the differential equation for its electromotive force rests only upon the two laws of thermodynamics. The thermodynamic derivation, however, involves the assumption that the only matter transported when a current is passed through is the ions, and it must be recalled that the ions whose activity is measured are the anhydrous ions. Washburn¹⁰ has definitely established that there is also a transport of water. If we follow the method of Lewis and Randall, taking this into account and changing at the end from free energies to activities, we obtain for the electromotive force of a cell with electrodes at which the anion reacts,

$$E = -\frac{RT}{F} \left[\int_{A}^{B} t_{+} \, d \ln (a_{+} \times a_{-}) + \int_{A}^{B} t_{w} \, d \ln a_{w} \right],$$

where the a's are activities, and the t's transport numbers, or the number of moles carried in the direction of the positive current when 1 faraday of electricity is passed through the solution. The subscript w refers to water, the others to the ions, and A and B to the two solutions.

An idea of the magnitude of the second term may be obtained from the measurements of MacInnes and Beattie⁹ on lithium chloride solutions

⁸ Hitchcock, J. Gen. Physiol., 5, 383 (1923). I wish to acknowledge my gratitude to Dr. Hitchcock for the use of some unpublished calculations and for calling my attention to some results of Fales and Vosburgh.

⁹ MacInnes and Parker, This Journal, 37, 1445 (1915). MacInnes, *ibid.*, 37, 2301 (1915). MacInnes and Beattie, *ibid.*, 42, 1117 (1920). Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 337.

¹⁰ Washburn, *ibid.*, **31**, 322 (1909).

if it is assumed that $t_{\rm w}$ is constant and equal to 1.5, the value found by Washburn for 1.28 M solution. The corresponding electromotive force is 0.14 mv. for a 0.1 M, and 5.35 mv. for a 3.0 M solution. The value of 308 for $t_{\rm +}$ in 1.28 M solution agrees well with 306 and 301 found by Washburn for the true transport number. Since there is no reason to suppose that $t_{\rm w}$ is really constant, $t_{\rm +}$ by this assumption should not equal the true transport number at other concentrations, and it does not seem worth while to publish the complicated calculations. Neglecting the transport of water, MacInnes and Beattie find excellent agreement between $t_{\rm +}$ and the Hittorf transport number, but the above argument shows that no exact relationship between these two quantities is thermodynamically established.

The magnitude of the effect of the transport of water in the potassium chloride-sucrose solutions may be estimated by integrating the equation assuming that t_+ is constant, and that $t_{\rm w}$ is, first, zero or, second, constant and equal to the value 0.6 found by Washburn. The mean activities calculated by these two assumptions are given in the second and third columns of Table II, on such a scale that the activity is unity in the solution without sucrose. The neglect of $t_{\rm w}$ makes a difference of about 10% in the most concentrated solution. Since we know nothing of the effect of sucrose on either t_+ or $t_{\rm w}$, and there is no reason to suppose that either is constant, we cannot even say that the activities lie between these two values.

TABLE II
ION ACTIVITIES IN SUCROSE SOLUTIONS

G. of sucrose Mean activity KCl		$a_{\rm Cl}$	$a_{\rm H}$		
per liter	$t_{\rm w}=0$	$t_{\rm w} = 0.6$	in HCl	in HCl	N/N_0
0	(1.00)	(1.00)	(1.00)	(1.00)	(1.00)
100	1.06	1.07	1.12	1.20	1.08
200	1.14	1.16	1.26	1.44	1.19
300	1.21	1.24	1.41	1.74	1.33
400	1.31	1.36	1.59	2.09	1.49
500	1.41	1.49	1.80	2.50	1.71
600	1.52	1.64	2.07	3.00	1.97
700	1.66	1.84	2.38	3.60	2.31

The fourth and fifth columns of Table II give the activities of chloride ion and of hydrogen ion in hydrochloric acid determined with a saturated potassium chloride bridge. The chloride-ion activity increases much more rapidly than the mean activity of the ions of potassium chloride calculated upon the above assumptions, and the hydrogen-ion activity increases still more rapidly. It may be noted that, if we assume that the chloride-ion and hydrogen-ion activities are really equal, all the discrepancies between Cols. 4 and 5 must be attributed to the liquid-junction potential, which leads to a difference of 5.3 mv. between the liquid-junction potentials of sat-

urated potassium chloride with $0.1\ N$ hydrochloric acid when there is no sucrose present, and when there is $700\ g$. per liter.

The following argument indicates that it is at least reasonable to assume that the saturated potassium chloride bridge does give constant liquidjunction potentials with varying sucrose concentration. There are two important reasons for the deviation of the activities of the ions from proportionality to their mole fractions which, in dilute solutions of the univalent chlorides, seem to exceed greatly the total of other more specific effects. The first is the effect of the electrical charges upon each other, which depends upon the total ionic concentration (not mole fraction) and upon the dielectric constant of the medium. In these solutions the concentration of salt is constant and the dielectric constant probably varies but little. If we assume that it is constant, the concentration of the ions and the effect of this factor will be constant. The second factor arises from the fact that our measurements give the activities of the unhydrated ions. The fraction of ions not hydrated may be extremely small, but any change in this fraction will give a corresponding change in the activity coefficient. Since the ions probably vary both in the stability and the complexity of their hydrates this effect will be specific for the various ions. It will be a function of the activity of the water, and should not be measurable until that activity becomes appreciably less than that of pure water. It offers the simplest explanation of the unequal activities of ions and the increase of activity coefficients with concentration in concentrated solutions. behavior of the metallic chlorides indicates that this factor is very small for the chloride ion. If it is zero, the activity of the chloride ion should be proportional to its mole fraction in these solutions. Any effect of this factor would be to make the activity increase more rapidly than the mole fraction as the concentration of sucrose is increased. The last column of Table II gives N/N_0 for either ion, calculated by the equation, N/N_0 = $[55.5 + 0.2]/[C_s/(1 - a_w) + 0.2]$, where N and N₀ are the mole fractions with and without sucrose, C_s is the concentration of sucrose in moles per liter, and a_w is the activity of water in a solution containing the same proportion of sucrose and water but not salt. The use of this formula assumes that the solution is ideal with respect to water except for the hydration of sucrose, and that no appreciable fraction of the water is used to hydrate the ions at such dilutions. The values are only a little smaller than the measured values of the chloride-ion activity in hydrochloric acid, indicating a small decrease in hydration and offering some confirmation of the assumption that the liquid-junction potential is independent of the sucrose concentration.

According to these hypotheses the increase in the ratio of activity to mole fraction for the hydrogen ion is due to an increase in the fraction of unhydrated ion with decreasing activity of the water, whether this decrease is due to high concentrations of sucrose or of the acid itself. Whatever the cause is, it is obvious that the activity of the hydrogen ion is not proportional to its mole fraction or molality, and that it cannot be used legitimately to calculate the extent of hydration. The fact that the activity of hydrogen ion in acetic and in sulfuric acids increases less rapidly than in hydrochloric acid may be accounted for most simply by assuming that the dissociation of these acids decreases as the sugar concentration increases. This decrease may be explained, at least semi-quantitatively, by the increase in the mole fraction without any variation in the ionizing power of the solvent.

The confirmation of the elimination of liquid-junction potential with sucrose solutions is not too reassuring, but even this cannot be extended to the addition of another solute in general. Analysis of Planck's differential equation for liquid-junction potentials indicates that the potential depends upon both the activity and the conductivity of the ions, and probably also upon their concentration. If these solutions the concentration remains constant, the activity increases, and the conductivity decreases still more rapidly. It is possible that these effects equalize one another in this particular case, but it is not probable that they would do so in general. The extension of the use of the saturated potassium chloride bridge to solutions in general seems very dangerous.

Summary

- 1. The proof of Fales and Vosburgh that the saturated potassium chloride bridge eliminates liquid-junction potentials depends upon the assumption that in a hydrochloric acid solution the activities of the 2 ions are equal. The proof of Corran and Lewis depends upon incompatible formulas for the electromotive forces at the 2 electrodes.
- 2. An analysis of experimental results indicates that the liquid-junction potential with saturated potassium chloride is not more than 1 millivolt for solutions less than $0.1\ M$ but that it increases rapidly with the concentration for hydrochloric acid.
- 3. There is some theoretical confirmation for the assumption that the liquid-junction potential with a saturated potassium chloride bridge is independent of the sucrose concentration if the concentration of electrolyte remains constant. This substantiation cannot be extended to solutes in general.
 - ¹¹ Lewis, Merriman and Moran, This Journal, 45, 702 (1923).
 - 12 Jones and Lewis, J. Chem. Soc., 117, 1120 (1920).
- 13 I must disclaim any credit given me in Ref. 12 for originating the hypothesis that the increase in hydrogen-ion activity on the addition of another solute is due to increased ionization, which dates back at least to Loomis and Acree [Am. Chem. J., 46, 621 (1911)]. My contribution was to show that, if this effect were attributed to increased ionization, the ionization need not be more than 100% for sulfuric acid.

¹⁴ See also MacInnes and Yeh, This Journal, 43, 2563 (1921).

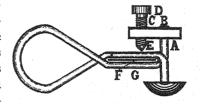
- 4. The ordinary thermodynamic formula for the electromotive force of a concentration cell with transport ignores the transport of water. If this be taken into account the transport number involved is the true and not the Hittorf number.
- 5. Emphasis is laid upon the fact that activity measurements give the activity of the unhydrated ion. An increase in the fraction of ions not hydrated gives the simplest explanation of the increase of activity coefficients in concentrated solutions.

AMHERST, MASSACHUSETTS

NOTES

A Screw Modification of the Mohr Pinch Clamp.—Although the use of a Mohr buret is often made imperative in volumetric work, no satis-

factory pinch clamp has ever been devised to allow dropwise delivery of solutions from a buret of this type. The accompanying sketch shows the details of a pinch clamp designed to fill this need. It may easily be made from an ordinary Mohr clamp, and has an advan-



tage over a screw clamp in that only one hand is required for its manipulation.

Into a brass plate 3 mm. thick, 1 cm. wide, and 2 cm. long 2 holes, B and C, are drilled and then tapped. The wire A leading up from the jaws of the clamp is threaded, screwed into the plate through B, and then brazed or soldered securely in the position shown in the figure. A large-headed brass screw D is then screwed through C until its pointed end E just touches the top of plate F when the clamp is pressed just hard enough to allow liquid to pass in drops through the rubber tube between plate F and wire G. Of course, by screwing D further it is possible to secure any other desired rate of flow.

DEPARTMENT OF CHEMISTRY
THE RICE INSTITUTE
HOUSTON, TEXAS
Received February 10, 1923

WILLIAM M. CRAIG

Gas Electrode.—A convenient form of hydrogen or other gas electrode and one which attains the equilibrium value very quickly, may be made as follows. A piece of round graphite rod A of any convenient size (3 mm. diameter was used) is drilled axially to within 6 mm. of the bottom. This is attached to a similar sized copper tube B, for leading in the gas, by a short length of rubber tubing C as shown in the figure. A spiral of light

copper or platinum wire D, inserted as shown, ensures electrical contact between the copper and graphite. The outside surface of the graphite is then platinized in the usual manner. When gas at $^1/_4$ to $^1/_2$ of an atmosphere is forced in, it passes very slowly and uniformly through the graphite forming small bubbles over the entire surface, thus very quickly saturating the platinum black and using a minimum quantity of gas. Such an electrode supplied with hydrogen from a cylinder came to the equilibrium value within $1^1/_2$ minutes and remained constant even though the electrode was in an open beaker of acid. This type of electrode is being used at this Laboratory for measurement of the reduction potential of acetylene and ethylene mixtures and is found to come to an equilibrium very much more quickly than a platinized platinum electrode and to

require less gas. A glass tube can of course replace the copper tube, and the light spiral wire be carried through a seal further up the tube.

Wilke² tried to use a palladium tube as a hydrogen electrode in the same way as the graphite electrode described above, but found the electromotive force was dependent on both the internal and external pressures. This effect was not observed with the graphite electrode; a higher pressure only caused the electromotive force to reach equilibrium sooner. There is an essential difference between the two electrodes; the graphite is actually porous but Wilke believes the hydrogen must diffuse through the palladium. There is reason³ to believe that it is monatomic hydrogen which passes through the electrode in the latter case and there may exist, therefore, on the outer surface of the palladium a slight excess of monatomic hydrogen over its equilibrium concentration. This would cause the electromotive force to be higher and to increase with increase of pressure. In the case of the graphite the diatomic hydrogen passes through and has at the surface a pressure of 1 atmosphere. The platinizing on the surface very materially stabilizes the elec-

tromotive force, and the opinion is ventured that if the palladium tube were platinized it would catalyze the formation of diatomic from the excess monatomic hydrogen and give correct values for the electromotive force dependent only on the external pressure.

Rogers Laboratory of Physics Electrochemical Laboratory Massachusetts Institute of Technology Cambridge 39, Massachusetts Received May 9, 1923 M. KNOBEL

¹ Measured only to 0.1 mv.

² Wilke, Z. Elektrochem., 19, 857 (1913).

³ See the work of Winkelmann, Ann. Physik, 6, 104 (1901).

Tetramethylammonium Tri- and Tetrachloro-iodides.—Weltzien¹ describes the preparation of the di-, tri- and tetrachloro-iodides of tetramethylammonium. No polyhalides of ammonium or the alkali metals corresponding to tetramethylammonium trichloro-iodide, N(CH₃)₄ICl₃, are known; it was, therefore, thought desirable to repeat Weltzien's work.

Analysis of the solid obtained by the method which Weltzien supposed to yield the trichloride gave results which were low and variable, so that the existence of this compound does not appear to be satisfactorily established; probably it is a mixture of the di- and tetrachloro-iodides produced by the partial decomposition of the latter substance.

Weltzien's analysis of the tetrachloro-iodide showed that his product was partly decomposed. A solid more closely approaching the composition of tetramethylammonium tetrachloro-iodide, N(CH₃)₄ICl₄, is obtained by the long continued action of dry chlorine gas on tetramethylammonium iodide at 28°. The solid was weighed in a small glass-stoppered weighing bottle, with glass inlet and outlet tubes also fitted with ground glass stoppers. A slow, continuous stream of chlorine was conveniently obtained by the electrolysis of a concd. solution of hydrochloric acid, the gas was passed through water and concd. sulfuric acid and then into the bottle containing the iodide; the latter first turned brown, then black and finally was completely converted into an orange-colored solid. The bottle was weighed from time to time with the following results:

Expt. 1. 0.5173	g. of iodide used	Expt. 2. 0.6	030 g. of iodide used
Time: days	Gain: G.	Time: days	Gain: G.
2	0.0898	38	0.3522
14	0.1874	51	0.3779
29	0.2739	77	0.3820
52 (constant)	0.3616	99 (constan	nt) 0.4244
Total gain 69.9%		70.4%	

The formation of N(CH₃)₄ICl₄ requires a gain of 70.6% in weight The substance formed in Expt. 1 was analyzed; 0.8484 g. required 140.48 cc. of 0.0694 N arsenite equivalent to 0.3457 g. of chlorine or a gain in weight of 68.8 %.

CEYLON UNIVERSITY COLLEGE WILLIAM NORMAN RAE
COLOMBO, CEYLON
Received December 14, 1922

Some Solidification Curves of Binary Systems.—In a series of papers on the solidification points of binary systems of various nitro derivatives of toluenes by Professor Bell,¹ I am erroneously attributed with having in my prior researches² taken as the temperature of solidification of binary

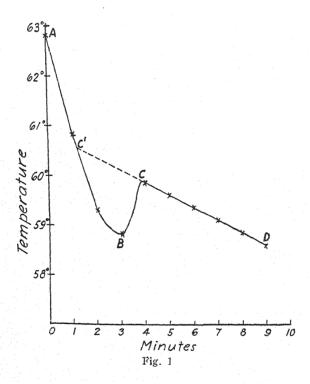
¹ Weltzien, Ann., 99, 1 (1856).

¹ Bell, J. Ind. Eng. Chem., 11, 1124 (1919).

² Giua, Ber., 47, 1718 (1914). Gazz. chim. ital., 45, 339 (1915).

mixtures the minimum obtained as the effect of supercooling. Since this opinion is repeated by C. A. Taylor and W. H. Rinkenbach,³ in order that the American reader may not gain the impression that I am ignorant of the most elementary rules for the determination of the point of solidification (though my book, "Chemical Combinations between the Metals," should be sufficient to demonstrate the contrary) I have replied to Professor Bell in the Gazzetta chimica Italiana⁴ and to Messrs. Taylor and Rinkenbach in the Giornale di chimica industriale ed applicata.⁵

I have to state that in the solidification curve, Fig. 1, as described by Professor Bell, I have taken the point C and not the point B as the temper-



ature of solidification. The discrepancy between my results and those of Professor Bell are due to his having taken the point C' as the solidification point. While my results are *experimental*, Professor Bell's are *extrapolated*. That my results are correct can be deduced also from the excellent investigation of A. L. Macleod, M. C. Pfund and M. L. Kil-

³ Taylor and Rinkenbach, This Journal, **45**, 44 (1923). *Ind. Eng. Chem.*, **15**, 73 (1923).

⁴ Vol. II, p. 101, 1923.

⁵ February, 1923.

patrick⁶ who refer directly to my researches and demonstrate that Professor Bell's correction is unnecessary.

LABORATORY OF ORGANIC CHEMISTRY
ROYAL POLYTECHNIC INSTITUTE
TURIN, ITALY
Received March 26, 1923

MICHELE GIUA

In the preceding note Professor Giua states that in his experimental data he has taken the point C of the diagram as representing the freezing point of a binary mixture. In his Italian and German articles to which reference has been made he labels the recorded temperatures as "beginning of crystallization." The beginning of crystallization obviously comes at the point B, and the rise in temperature from B to C is a result of crystallization which has followed supercooling. The confusion which has arisen comes, therefore, from the misnaming of temperatures which should have been called "maximum temperatures after crystallization" and not "temperatures of the beginning of crystallization."

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA
Received April 21, 1923

JAMES M. BELL

An Intercepted Hydrolysis.—In one of a series of experiments designed to bring about the formation of phosphonium cyanide, potassium cyanide was heated with stick phosphorus and a little water, in an atmosphere of hydrogen. The free caustic potash in the solution of potassium cyanide was expected to react with the phosphorus to give phosphine, the corresponding amount of liberated hydrogen cyanide providing an opportunity for combination. The gases evolved were passed over warm phosphorus pentoxide, and a white, crystalline product was collected in a cooled receiver. On analysis, this substance proved to be a very pure sample of ammonium cyanide, containing no phosphorus whatever.

The history of the reaction must be as follows. At ordinary temperatures, in a closed vessel, we have the equilibrium, $KCN + H_2O \longrightarrow KOH + HCN$. At higher temperatures, this equilibrium is destroyed by the disappearance, through further hydrolysis, of the hydrogen cyanide, $HCN + 2H_2O = NH_4OOCH$, which is a *complete* action, the ammonium formate being destroyed by the equivalent potassium hydroxide formed: $KOH + NH_4OOCH = NH_3 + HCOOK + H_2O$. In sum, $KCN + 2H_2O = NH_3 + HCOOK$, and when potassium cyanide is boiled with water, nearly all of the gas evolved is ammonia.

When phosphorus is present the hydrolysis is interrupted to an extent defined by the reaction of the phosphorus with the potassium hydroxide

⁶ Macleod, Pfund and Kilpatrick, This Journal, 44, 2260 (1922).

present, an equivalent amount of hydrogen cyanide being liberated. With a large excess of water, we should probably have $3KCN+4P+12H_2O=3KH_2PO_2+PH_3+3HCOONH_4$, but this excess is not present, and after a small amount of ammonium formate has formed, we reach equilibrium and hydrogen cyanide is liberally evolved.

There is, thus, a main reaction, $KCN + 2H_2O = NH_3 + HCOOK$, and a subsidiary reaction, $3KCN + 4P + 6H_2O = 3KH_2PO_2 + PH_3 + 3HCN$. We refer to them in this manner because the ammonia evolved was always in excess over the hydrogen cyanide.

The experiment was repeated with other non-volatile substances, reactive with potassium hydroxide. Aluminum powder, in place of phosphorus, also produced ammonium cyanide of great purity. A greatly superior yield, however, was obtained by using a suitable proportion of sulfuric acid. Attention was called in this case to the great readiness with which ammonium cyanide is oxidized. In the first trials of the sulfuric acid method, hydrogen was neither formed in the reaction (as in the case of aluminum) nor flushed through the apparatus (as in the case of phosphorus). The product was ochreous in appearance, and was sublimed only with difficulty. The cause of this proved to be the formation of a matrix of azulmic acid, produced, we think, as follows.

 $2NH_4CN + O = 2NH_3 + C_2N_2 + H_2O. \quad NH_4CN \rightleftharpoons NH_3 + HCN \\ 2NH_3 + 2C_2N_2 = C_4H_6N_6 \ (Hydrazulmin). \quad C_4H_6N_6 + H_2O = C_4H_6N_6O + NH_3.$

It has often been remarked that while ammonia is effectively administered in cases of prussic acid poisoning, ammonium cyanide is powerfully poisonous. As, however, this substance cannot exist at the temperature of the body, its effects are probably due to the formation of cyanogen, as shown above, through a damp oxidation. Ammonium cyanide is most readily ignited, burning with a pale, fawn-colored flame. It immediately decolorizes neutral potassium permanganate solution: when the latter is added drop by drop until the decolorization is slow, a vivid yellow solution is formed, and this does not become brown nor deposit hydroxides until after standing exposed to the air for many hours.

Similarly, ammonium cyanide is reactive with sulfur. When it is dissolved in a chloroform solution of sulfur, thin leaves of ammonium thiocyanate separate on partial evaporation.

Contribution from the Victoria University of Manchester Manchester, England Received April 18, 1923 OLIVER C. DE C. ELLIS LESLIE B. GIBBINS [Contribution from the Forest Products Laboratory, Forest Service, United States Department of Agriculture]

THE ACTION OF CONCENTRATED HYDROCHLORIC ACID ON DIFFERENT CELLULOSES

By E. C. Sherrard¹ and A. W. Froehlke² Received September 27, 1922

Introduction

When white spruce wood is hydrolyzed with dilute acid at atmospheric pressures, or higher, one of the reducing sugars produced is mannose. Some investigators have assumed that mannose is present in the wood as a mannan; others consider it to be present as a part of the cellulose. Sherrard and Blanco have further shown that in such a hydrolysis the quantity of sugar produced corresponds very closely with the quantity of cellulose removed. This would indicate that the mannose is present as a mannose cellulose. Recent investigation has brought to light the fact that mannose is contained in α , β and γ cellulose obtained from spruce cellulose prepared by the Cross and Bevan method. The same investigators have demonstrated that no mannose is present in cotton, and also that the reagents involved in the isolation of the celluloses from white spruce are not responsible for its formation.

The fact that white spruce cellulose on hydrolysis yields considerable quantities of mannose and that cotton yields no mannose on hydrolysis was considered ample proof that considerable difference exists between these two celluloses. In order to investigate further any possible differences in celluloses from different woods it was decided to submit several to the action of concd. hydrochloric acid and to observe the rate of change of optical rotations. Accordingly, celluloses from 2 softwoods, white spruce and Douglas fir, and one hardwood, yellow birch, were prepared by the method of Cross and Bevan and compared with cotton which had received the same treatment.

Experimental Part

The 3 species of wood used in this investigation were ground and screened. Only that which passed through an 80-mesh and was retained by a 100-mesh sieve was used. The material was placed in alundum

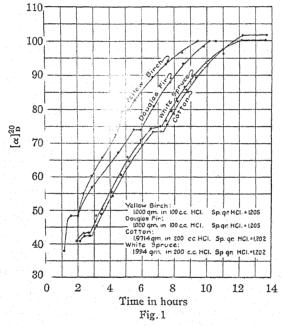
- ¹ Chemist in Forest Products, Forest Products Laboratory, U. S. Forest Service Madison, Wisconsin.
- ² Taken from a dissertation by A. W. Froehlke submitted to the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science.
 - ³ This Journal, 45, 1008 (1923).
 - 4 Schorger, J. Ind. Eng. Chem., 9, 748 (1917).
 - ⁵ Bertrand, Compt. rend., 129, 1025 (1899).
 - ⁶ J. Ind. Eng. Chem., 13, 61 (1921).
 - 7 Ref. 3, p. 1012.

crucibles and extracted in a Soxhlet extractor with an equal mixture of alcohol and benzene for a period of 4 hours. The excess of solvent was removed by suction, the residual alcohol and benzene washed out with boiling water, and the extracted material then dried over a water-bath.

The cellulose samples were prepared from these by means of the Cross and Bevan process as modified by Schorger.⁸

The same process was duplicated in the case of raw, ginned cotton wool so that any variation in the hydrolysis curves for cotton and the wood celluloses could not be attributed to a variation in the preliminary preparation of the celluloses.

In order to bring cellulose into solution in hydrochloric acid it is necessary to increase the acid content to 40% or greater. This was accomplished by passing hydrogen chlo-



ride through ordinary coned. hydrochloric acid cooled to -10° . The acid so made was tightly stoppered in a glass-stoppered flask and maintained at a temperature of 0° or lower until used. The strength of the acid was determined by means of specific-gravity determinations. For this purpose an hydrometer calibrated between 1.180 and 1.240 was employed.

It was found undesirable to use an acid of higher concentration because when the temperature of such an acid was raised from 0° to —20° considerable hydrogen chloride was evolved, making it unsafe to bring the acid to the required temperature in a closed flask.

Two hundred cc. of hydrochloric acid prepared as above was added to about 2 g. of the prepared cellulose in a glass-stoppered flask. The flask was tightly closed and the mass vigorously shaken until the cellulose completely dissolved.

⁸ Schorger, J. Ind. Eng. Chem., 9, 561 (1917).

In a preliminary experiment the curves of specific rotation plotted against the time showed a break common to the 4 celluloses at about the twelfth hour. tained a similar break between the second and third hours. The question immediately arose as to whether any relationship existed between the break in the curve obtained by Willstätter at the second hour and the break obtained in the curves of the hydrolysis of the 4 celluloses at the twelfth hour. Consequently, the 4 celluloses were hydrolyzed with a 41% hydrochloric acid and the course of hydrolysis followed from the first hour until a constant optical rotation was obtained; the following quantities of cellulose in 200 cc. of acid were used: 1.9714 g. of cotton cellulose, 1.9940 g. of white spruce cellulose, 2.0000 g. of Douglas fir cellulose, and 2.0000 g. of vellow birch cellulose. The cotton cellulose dissolved to a colorless solution in 20 minutes, which changed after 1.5 hours to a light straw-yellow, at about the fourth hour became much darker, and after 25 hours was light brown. The white spruce cellulose also required 20 minutes' shaking with the acid to complete its solution. This light brown solution became markedly deeper in color at about the fourth hour and after 25 hours the color was medium brown. The Douglas fir cellulose gave a colorless solution after 45 minutes' vigorous shaking. The particles before solution were very light brown while in contact with the acid. After 1.75 hours a trace of light yellow developed which became gradually darker. The yellow birch cellulose dissolved in 30 minutes to give a light brown solution.

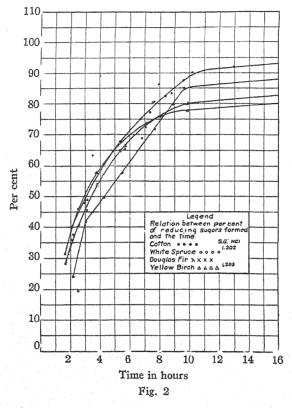
The change in specific rotation that occurs with time is illustrated in the curves of Fig. 1. The position of the curve is greatly influenced by the strength of the acid used, the rate of hydrolysis increasing as the concentration of the acid is increased so that the effect of a stronger acid on the curve is to displace it to the left.

Willstätter showed that the specific rotation of a solution of pure glucose in fuming hydrochloric acid is much greater than in water. To repeat this work, a 1% glucose solution in hydrochloric acid and water at 20° was prepared, the initial rotation readings were immediately taken, and the mutarotation was followed until no further change was observable. After 4.5 hours the glucose acquired a constant specific rotation of 51.81° in water, while in the 41% hydrochloric acid this amounted to 100.16° after 3 hours. Assuming that glucose is the only sugar formed on hydrolysis of cellulose and that it is formed quantitatively, the yields from the 4 celluloses determined by the known formula, $C = \frac{100\alpha}{1.(\alpha)_D}$, were found to be cotton cellulose, 91.40%; white spruce cellulose, 90.58; Douglas fir cellulose, 90.10; and yellow birch cellulose, 90.10.

During the progress of the hydrolysis, samples were periodically removed from the flask, diluted, neutralized and the content of reducing sugar was determined by means of Fehling solution. These results are plotted in Fig. 2.

The first few 5cc. samples removed for analysis by reduction with copper became turbid when they were diluted to 20 cc. with water. A light precipitate of cellulose settled on standing, the amount of which gradually decreased until after the fifth hour dilution no longer caused precipitation of cellulose. Those samples, which became turbid were filtered before analysis.

No direct relationship is evident between the values obtained by the polariscope and those by reduction of Fehling solution. The curves obtained by the latter method are smooth and increase rapidly until the tenth hour. The reaction then becomes much slower and a maximum is reached



only after about 25 hours. The values for dextrose obtained from the different celluloses by the reduction of Fehling solution are as follows:

			Douglas fir	Yellow birch
Time, h., m	22:55	22:50	25:20	25:20
Reducing sugar, %	97.8	93.9	87.57	85.60

Theory and Discussion

In the curves where specific rotations at 20° are plotted against time it is seen that those for spruce cellulose and cotton are practically identical regardless of the presence of mannose in the former. However, distinctly different curves were obtained for Douglas fir and yellow birch, the difference lying in the fact that the specific rotation of the yellow birch rises much more rapidly than that of any of the other celluloses used. A marked difference in the case of yellow birch was expected since it

contains about 28% of pentosan⁴ as compared with 5.5% and 9.5% for Douglas fir and white spruce, respectively. Further, the curves for all 3 wood celluloses are distinctly different from one another and with the exception of spruce cellulose are quite different from that for cotton.

An interesting relationship exists between all 4 curves. It will be noted that 2 breaks in the curve are common to each cellulose, the first break occurring at about the second hour, and the second one at about the sixth or seventh hour. Willstätter and Zechmeister9 call attention to the first break in the curve for cotton as indicated between the second and third hour but neglected to take readings often enough between the seventh and eighth. They attribute the first break to the intermediate formation of cellobiose. This idea, however, is open to question. From a consideration of the last curves, showing optical rotation, apparently three reactions occur. These sharply defined stages of the reaction may indicate successive steps in the conversion of the cellulose to the final products or to secondary reactions of the products among themselves or with the hydrochloric acid. They may also be due to changes in the optical activity of the liberated sugars. It may also be assumed that from the start of the reaction 3 sugars are simultaneously formed. Under these circumstances the observed rotation would be the sum of the rotations of the individual sugars. If at some intermediate point along the curve the formation of one of the sugars ceases and its specific rotation becomes constant then a break in the curve would be produced such as was obtained experimentally. When it is assumed that 3 sugars act in this manner at 3 different points on the curve, then specific rotation curves would be produced having breaks identical in character with those obtained experimentally. On the other hand, instead of having several reactions taking place simultaneously, it would be entirely feasible to look upon the specific-rotation curves as resulting from a number of successive reactions. In this case the initial product would be a sugar whose rotation becomes constant after several hours, because after that time the sugar is no longer a reaction product. Just at this time another reaction results in which another sugar is formed. This reaction proceeds as in the case of the first sugar formed. If a third reaction of this nature occurs, then again a curve is produced having breaks corresponding to those obtained experimentally.

From the curves which illustrate the rate of formation of reducing sugars it may be seen that the amount of sugar formed gradually increases. The slope of these curves toward the end of the reaction is not as great as the slope during the initial course of the hydrolysis. This may be attributed to a slight reduction in the acid concentration of the solution. Although every precaution was taken to prevent any loss in the acid content of the cellulose solution during hydrolysis, it is recognized that in the

Willstätter and Zechmeister, Ber., 46, 2401 (1913).

frequent handling of the solution some loss in hydrogen chloride was involved, but it is believed that this loss was negligible.

Conclusion

The curves showing the specific rotation for celluloses from spruce, yellow birch, Douglas fir, and cotton in solution in coned. hydrochloric acid, exhibit marked differences, indicating a difference in either the primary or the secondary reactions, which in turn would point to a difference in the celluloses, themselves.

A marked similarity was observed between the curves for cotton and white spruce celluloses. It is known that cotton hydrolyzes only to glucose, while a large percentage of the sugar formed by the hydrolysis of white spruce is mannose, which has a much smaller specific rotation than glucose, so that the solution of hydrolyzed white spruce should show a lower specific rotation than that of cotton cellulose. The curves for cellulose from Douglas fir and yellow birch are also similar in character, although the former contains 5.5% of pentosan while the latter contains as high as 28% of pentosan. This great variation in composition should cause a distinct difference in the specific rotations, but such is not the case, as may readily be seen from the curves.

In view of these facts we are forced to admit with Cunningham¹⁰ that the optical method for determining the quantitative conversion of cellulose to sugar is of little value. It does, however, indicate that considerable differences exist between celluloses from different sources; otherwise, all the curves would be identical in shape.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SOUTH DAKOTA]

THE ISOSTERISM OF PHENYL ISOCYANATE AND DIAZOBEN-ZENE-IMIDE

By WALLACE H. CAROTHERS Received October 23, 1922

It was the purpose of the investigation the results of which are reported in this paper to test experimentally a prediction arising from the octet theory of the structure of atoms and molecules.

The structural formula of phenyl isocyanate is usually represented as C_6H_5 —N=C=O (1), and of diazobenzene-imide as C_6H_5 —N=N=N (2), or as C_6H_5 —N=N (3). Applying the principles of the theory of atomic

structure originated by G. N. Lewis¹ these would be C₆H₅:N::C::O:

¹⁰ Cunningham, Trans. Chem. Soc., 113, 173 (1918).

¹ Lewis, This Journal, 38, 762 (1916).

(1A),
$$C_6H_5:N::N::N:$$
 (2A), and $C_6H_5:N:::$ (3A). If it is assumed that the

azo-imide has the structure 2A and the isocyanate the structure 1A then these 2 molecules have the same number of extra nuclear electrons arranged in the same way and differ only in the magnitude of the nuclear charges of some of the atoms. They should, therefore, be very similar in their physical properties. Langmuir³ who pointed out this implication of the

² Since the validity of one of the conclusions of this paper depends upon the justness of the assumption that no other structures than 1A, 2A and 3A are probable for these 2 substances, it may be well to present some arguments in defense of this assumption. The valences here concerned are typically non-polar so that 1A, 2A and 3A may be rep-

resented as R—N=C=O (1B), R—N=N=N (2B) and R—N
$$\stackrel{N}{\parallel}$$
 (3B), and these

formulas will have the same significance as ordinary structural formulas with the added significance that each bond represents a pair of electrons shared between 2 atoms.

Other formulas are possible, such as R—N
$$\equiv$$
N—N, R—N $\stackrel{\sim}{=}$ N, R—N—N \equiv N for the

azo-imide, and R—N=C—O, R—N
$$\stackrel{C}{=}$$
, R—C—N=O, R—O=C=N, etc., for the

isocyanate. To decide among the possibilities, the chemical evidence is examined, and leads to Formulas 1, 2, and 3, of which 1 and 3 may be represented by identical formulas 1B and 3B in terms of the octet theory, and the second by R—N—N (2B).

The question now is whether any of these possible structures other than 1B, 2B and 3B is consistent with the chemical evidence.

It might be thought that the familiar reactions of the isocyanates with R'OH, $R'NH_2$, etc., could be represented by $R-N\equiv C-O$. This is true. But the acceptance of this formula involves one of two assumptions: (a) the urethans and ureas have the formulas R-NH=C(-O)-OR' and R-NH=C(-O)-NHR' instead of the structures usually assigned to them, or (b) rearrangement of bonds takes place after the reaction. The usual formula, R-N=C=O, obviously has the advantage of simplicity and naturalness. Moreover, the formula $R-N\equiv C-O$ is inherently improbable on the basis of the octet theory itself. It represents the nitrogen atom as having completed its sheath by sharing more than 3 pairs of electrons and the oxygen atom as having completed its sheath by sharing only 1 pair of electrons; in the absence of any definite force necessitating such arrangement the substance should spontaneously rearrange into R-N=C=O in accordance with the principle that the "charge" on each atom tends toward a minimum [See Langmuir, *Science*, 54, 59 (1921)].

The corresponding formula, R-N = N-N, for the azo-imide is still less satisfactory. It conflicts still more violently with the principle above mentioned, and for the same reason would spontaneously rearrange into R-N=N-N. Moreover, it scarcely represents any of the chemical properties of the azoimide. Thus, RN_3 reacts with R'Mg-Br to form R-N=N-NHR' [Ber., 38, 670 (1905); 39, 3905 (1906)], whereas the structure R-N=N-N requires that the R' be attached to the first or second nitrogen atom.

Of the other formulas for $R-N_3$ and RNCO possible on the basis of the octet theory, many are obviously entirely incompatible with the chemical evidence and all are less probable than those which have been considered in drawing the conclusions here presented.

³ Langmuir, This Journal, 41, 1543 (1919).

octet theory gave the name isosterism to this type of relationship between molecules. He presented evidence of the existence of isosterism between some pairs of gases and between numerous pairs of crystalline solids. Lack of sufficient data prevented complete verification of his prediction³ that cyanic and hydrazoic acids are isosteric; and no data have been presented on liquid isosteres. The lack of data on cyanic and hydrazoic acids is probably due to their instability. Some of the organic isocyanates and azoimides, which may be regarded as derived from these acids are, however, much more stable; and as the phenyl derivatives are easily available and liquid at ordinary temperatures, it was thought worth while to study some physical properties of these derivatives.

The densities, vapor pressures and viscosities were measured at various temperatures and the following values obtained.

Table I

Densities, Vapor Pressures and Viscosities of Phenyl Isocyanate and Phenyl
Azo-imide

A	bsolute Densi	ties	Vapor P	ressure in mn	1. of Hg.
Temperature C.	PhNCO	PhN ₃	Temperature C.	PhNCO	PhN ₃
0.0	1.1152	1.1175	75.0	36.3	33.8
10.0	1.1049	1.1070	80.0	45.3	41.8
20.0	1.0943	1.0968	85.0	55.9	52.0
30.0	1.0840	1.0864	90.0	68.2	63.6
40.0	1.0736	1.0762	95.0	83.9	79.1
50.0	1.0630	1.0657			
Viscos	sities in Centip	ooises	Visc	osities in Cer	itipoises
0.0	1.326	1.479	25.0	0.899	0.956
11.0	1.111	1.205	30.0	0.834	0.887
16.0	1.024	1.106	35.0	0.779	0.827
20.0	0.963	1.033	40.0	0.739	0.775

When these properties are plotted against the temperatures, smooth graphs are obtained and in each case the two curves are almost exactly parallel. The data may be summarized by means of conventional algebraic equations; t is the temperature.

```
Densities
Phenyl isocyanate
Diazobenzene-imide
Vapor Pressures
Phenyl isocyanate
Phenyl isocyanate
Diazobenzene-imide
Viscosities
Phenyl isocyanate
Phenyl isocyanate
Viscosities
Phenyl isocyanate
Pi = 1.326 - 0.02163t + 0.000174t^2, where t' = t - 1.326.

t = 1.326 - 0.02163t' + 0.000174t^2, where t' = t - 1.326.
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The agreement between the values calculated by these formulas and the experimental ones is in each case practically within the limits of experi-

mental error, which for the densities is about $\pm 0.03\%$, and for the viscosities and vapor pressures about $\pm 0.7\%$.

The properties of the isocyanate at any given temperature are thus the same as those of the azo-imide at temperatures from 1.7° to 4.8° higher, which is in accordance with the prediction. It is interesting to note also that the disparity between the properties of the two compounds is the same in type and degree as in the properties of the gaseous isosteres which Langmuir originally used to verify the principle of isosterism. The data here presented, then, confirm this principle. Incidentally they also confirm the straight-chain structure for triazo compounds, except that these should probably be written as R-N=N=N as Langmuir predicted instead of as R-N=N=N=N.

Experimental Part

Diazobenzene-imide was prepared by the method of Fischer' as modified by Dimroth.⁸ It was washed with dil. hydrochloric acid and sodium hydroxide several times, then with water, dried with calcium chloride, distilled under diminished pressure, treated with sodium and fractionated under diminished pressure into a Brühl receiver desiccated with phosphorus pentoxide. The phenyl isocyanate was a commercial sample prepared, presumably, from phosgene and aniline. It was treated with sodium and fractionated in the same way. Thus purified, it was water-white and developed no precipitate or turbidity after a month, even when occasionally exposed to the air.

Densities were determined by means of a pycnometer. Vapor pressures were determined by means of the static isoteniscope of Smith and Menzies. The manometer was a simple U-tube 1 meter long and about 8 mm. in internal diameter fastened to a meter stick and made vertical. Readings were made with the naked eye by means of a mirror. The viscosities were determined with a Washburn viscosimeter made from ordinary glass. Times of flow were determined simultaneously by means of 2 stopwatches, from 4 to 8 readings being made at each temperature. All the data represent the means of various determinations, at least 2 different, freshly purified samples being used in each case. The temperatures were regulated by hand to about 0.05° during

 $^{^4}$ The calculated value for the viscosity of the azo-imide at 0° differs from the experimental value by about 3.6%, but since this calculation is equivalent to an extrapolation of the isocyanate curve into a region where the viscosity is changing very rapidly, the disagreement can hardly be considered as serious.

⁵ Langmuir, This Journal, **42**, 285 (1920).

⁶ The structure R—N≡N is, of course, impossible from the point of view of the octet theory. The straight-chain structure for triazo compounds has been proposed and supported by Turrentine [This Journal, 34, 385 (1912); 36, 23 (1914)], by Thiele [(Ber., 44, 2522 (1911)] and by Franklin [Proc. 8th Inter. Cong. App. Chem., 6, 119 (1912)] and the ring structure has been defended by M. O. Forster [ibid., 6, 108 (1912)].

⁷ Fischer, Ann., 190, 92 (1878).

⁸ Dimroth, Ber., 35, 1032 (1902).

⁹ Smith and Menzies, This Journal, 32, 1412 (1910).

¹⁰ Washburn, ibid., 35, 737 (1913).

¹¹ The viscometer was made of glass, and the water constant was determined at each temperature at which readings were made. In calculating the viscosities in centipoises from these readings the table of Bingham and Jackson [Bur. Standards Sci. Papers, 298, p. 75] of the viscosity of water was used.

the measurements of densities and vapor pressures, and automatically to 0.005° or better in the determination of the viscosities.

Summary

Assuming the atoms of phenyl isocyanate and of diazobenzene-imide to be arranged as indicated in the formulas, C_6H_5NCO and C_6H_5NNN , application of the octet theory leads to the conclusion that they are isosteric. They should, therefore, be very similar in their physical properties. Their densities, vapor pressures and viscosities have been measured at various temperatures, and this prediction confirmed. These results also confirm the straight-chain structure for triazo compounds.

CHEMICAL LABORATORY UNIVERSITY OF ILLINOIS URBANA, ILLINOIS

[Contribution from the Laboratory of Organic Chemistry of the State University of Iowa]

DIACYL DERIVATIVES OF ORTHO-HYDROXYBENZYLAMINE

By L. Chas. Raiford and E. P. Clark Received February 2, 1923

Previous work in this Laboratory has shown (a) that when 2-acetylaminophenol is subjected to the action of benzovl chloride (Schotten-Baumann reaction), the benzovl radical is attached to nitrogen while acetyl migrates of oxygen;1 (b) that this migration is not prevented by the presence of acid-forming substituents (halogen) attached to the nucleus of the aminophenol;2 (c) that the acetyl-benzoyl derivatives of p-aminophenols do not suffer this rearrangement; 3 (d) that the presence of bromine and other heavy radicals adjacent to the reacting groups (amino and hydroxyl), which in many reactions causes marked retardation, does not prevent the migration;4 and (e) that these observations seem to hold with bases derived from naphthalene, namely, 1-amino-2-naphthol and halogenated derivatives.⁵ Since the acetyl-benzoyl derivatives of more than 15 o-amino-phenols, having various substituents at different positions in the molecule, have been tested in this way and all have been found to undergo this migration, it may be assumed that this behavior is general for this class of compounds when the acyl radicals are those specified.

Although the migration of this kind has thus far been observed to take place only in the derivatives of compounds in which both reacting groups

¹ Raiford, This Journal, 41, 2068 (1919).

² Raiford and Couture, ibid., 44, 1793 (1922).

³ Raiford and Iddles, *ibid.*, 45, 469 (1923).

⁴ Woolfolk, unpublished report.

^b Armstrong, unpublished report.

(hydroxyl and amino) were attached directly to the benzene ring. Auwers and his students6 have reported a rearrangement in which acvl wandered from oxygen to nitrogen when oxygen was attached to the ring and nitrogen was on a side chain. Thus, when an O-acyl derivative of o-hydroxybenzyl bromide was heated with aniline, the bromine atom was replaced by the phenylamino radical and at the same time the position of the acyl shifted from oxygen to nitrogen; while McConnan and Titherly7 found that under certain conditions o-acylsalicylamide rearranged to N-acylsalicylamide, and that the change was reversible. The starting compounds in these cases were somewhat different from those heretofore employed in our work, in that in salicylamide not only was the amino radical on a side chain, but the carbon of this chain was in the form of a carbonyl group, while in the benzylamine used by Auwers and collaborators one of the amino hydrogen atoms was replaced by a hydrocarbon radical (phenyl or a homolog).8 Auwers' results, too, differed from ours to the extent that, with only one of the benzylamine derivatives he prepared, apparently, did he observe the migration of acyl from nitrogen to oxygen. In that instance the product was not stable, but rearranged spontaneously to the N-acyl derivative, which would be expected when the amino radical is not already acylated. On account of these differences, and also because of the sharply defined behavior of the products studied by the abovementioned authors, as well as the equally definite results of our own work, it became a matter of interest to study the behavior of acetyl-benzoyl derivatives prepared from a phenolic compound having an unsubstituted amino radical attached to a side chain adjacent to an hydroxyl group.

For this study o-hydroxybenzylamine, prepared as indicated below, was selected. With the exceptions noted in the Experimental Part, the preparation and hydrolysis of the derivatives of this base were carried out as described in previous papers. It may, however, be stated at once that benzoylation of o-hydroxybenzyl-acetamide did not cause the migration of the acetyl radical, and that the introduction of the acyl radicals in different orders gave isomeric acetyl-benzoyl derivatives; this is entirely

- ⁶ Auwers and others, Ber., 33, 1923 (1900).
- ⁷ McConnan and Titherly, J. Chem. Soc., 89, 1318 (1906).

⁸ In this connection it is to be noted that certain well-known rearrangements involving the amino radical do not take place when this hydrogen has been substituted by an alkyl or aryl radical. Thus, Slosson [Ber., 28, 3266 (1895); Am. Chem. J., 29, 295 (1903)] found that "the presence of the hydrogen atom (H⁺) of the acylamine halides, RCONH-Hal is essential for the successful Beckmann rearrangement," while Ransom, [Am. Chem. J., 23, 26 (1900)] proved that in the diacyl derivatives of methyl-o-aminophenol that he studied there was no molecular rearrangement. Stieglitz [Am. Chem. J., 29, 52 (1903)] formulated a theory to account for this behavior and, in addition to the cases cited above, has called attention to the fact that chloro-imido esters, whose parent substances are acid halogen-amides, and hydroxylamine derivatives that can no longer lose water, have lost the tendency to undergo a Beckmann rearrangement.

different from the behavior of such compounds when both the reacting radicals are attached directly to the aromatic nucleus.

Experimental Part

o-Hydroxybenzylamine.—Salicylaldoxime, used in preparing this amine, was obtained in excellent yield by following the general method of Loch⁹ modified by removing under reduced pressure practically all the alcohol used as solvent in the early part of the experiment, and mixing the residue with water before extraction with ether. The extract thus obtained was dried with anhydrous sodium sulfate, the greater part of the ether was distilled, and the residue allowed to crystallize. The product was purified by treatment of its chloroform solution with petroleum ether, which gave colorless crystals that melted at 57° as reported in the literature. Fifty g. of aldehyde gave 55 g. of oxime, a yield of 98%. Loch reported no yield.

To obtain the amine 10 20 g. of the oxime, purified as indicated above, was dissolved in 300 cc. of 50% alcohol and reduced in the usual way with 2.5% sodium amalgam. 11 The temperature was kept below 55° and the excess of alkali continually neutralized by the addition of hydrochloric acid. However, the reaction mixture was kept slightly alkaline to litmus until reduction had been completed. This was indicated by a copious evolution of hydrogen. The solution was then made slightly acid, separated from the mercury and evaporated under reduced pressure until sodium chloride began to crystallize. The residue was diluted with water and concentrated as before, in order to remove as completely as possible the alcohol previously used as solvent. The mixture was again diluted with water to a volume of about 300 cc. and transferred to an Erlenmeyer flask containing about 25 cc. of ether. Ammonium hydroxide was added in small portions until a slight excess was present. The mixture was shaken vigorously after each addition. Upon continued shaking for a few minutes the amine began to crystallize on the sides of the flask. After a short time, the product was removed by filtration. Extraction of the mother liquor with ether and evaporation of the solvent gave more of the

⁹ Loch, Ber., 16, 1782 (1883).

¹⁰ This amine had previously been prepared by Goldschmidt and Ernst [Ber., 23, 2740 (1890)] in accordance with Salkowski's method [Ber., 22, 2142 (1889)] by heating o-anisamine with hydrochloric acid under pressure for several hours. These workers stated that only a poor yield of the base could be obtained by reduction of salicylaldoxime with sodium amalgam, although several different modifications of the method were tried. They recorded 121° as the melting point of their product. Tiemann [Ber., 23, 3016 (1890)], who obtained this base by the reduction of salicyl-m-hydrazone-benzoic acid with zinc dust and dil. sulfuric acid, reported no yield but recorded a melting point of 125°. Auwers and Walker [Ber., 31, 3038 (1898)], who prepared it from o-cyanophenol by the Mendius reaction, reported neither yield nor melting point.

¹¹ This was prepared in accordance with Nef's method [Ann., 280, 307 (1894)] modified as follows: 25 g. of sodium in small pieces was added to 975 g. of purified mercury covered by 400 cc. of toluene in a 1-liter beaker and the mixture stirred constantly. This was most easily done by placing the pieces of sodium on a sharp pointed glass stirring rod and, forcing them under the surface of the mercury; the reaction took place at once. The toluene reached the boiling point before all the sodium had been introduced, but the latter was added quite rapidly toward the end. Finally the toluene was decanted, and the solid amalgam was gently heated in a casserole until it melted and became homogeneous. It was next freed from slag by pouring it slowly upon a large piece of paper, the slag remaining in the casserole. As soon as the pure product thus obtained was sufficiently cool to be handled, it was broken up and placed in a well-stoppered container.

crystals. In this way 20 g. of oxime gave 15.5 g. of amine by direct crystallization and 1.7 g. from the mother liquor, a total of 17.2 g. or a yield of 96%.

It was best recrystallized by treatment of a solution in absolute alcohol with petroleum ether. Purified in this way, it began to soften at 126° and melted at 129° (uncorr.). Analysis (Kjeldahl) indicated that it was pure.

Analysis. Subs., 0.2513: 20.25 cc. of 0.1 N HCl. Calc. for C_7H_9ON : N, 11.37. Found: 11.29.

o-Acetyloxybenzyl-acetamide.—Two g. of o-hydroxy-benzylamine was added slowly to a hot solution of 2 drops of concd. sulfuric acid in 8 g. of acetic anhydride, after which the mixture was boiled gently for 5 minutes and then allowed to stand for 2 hours. It was poured into water and neutralized with sodium hydrogen carbonate. The acetyl derivative was removed by extraction with chloroform, the solution dried and evaporated to a small volume, after which petroleum ether was added. The crystals weighed 2.8 g.; yield, 12 83%. Recrystallization by the same method gave hexagonal plates; m. p., $^{102-103}$ °. Analysis (Kjeldahl) indicated the presence of 2 acetyl radicals.

Analysis. Subs., 0.3041: 14.58 cc. of 0.1 N acid. Calc. for $C_{11}H_{13}O_{3}N$: N, 6.76. Found: 6.72.

o-Hydroxybenzyl-acetamide.—This compound, previously prepared by Goldschmidt and Ernst¹⁰ by direct acetylation, was obtained by hydrolysis of the diacetyl derivative described above. One g. of the latter was dissolved in 50 cc. of 95% alcohol containing slightly more than 2 molecular proportions of potassium hydroxide. The solution was allowed to stand for about 5 minutes, and then made acid to congo red with hydrochloric acid. Potassium chloride was removed, the filtrate evaporated under reduced pressure to a small volume, and 20 cc. of water added. This gave 0.59 g. of a crystalline product. The mother liquor was extracted with chloroform, the extract dried and reduced to a small volume, and petroleum ether added. A further quantity of substance, 0.21 g. was obtained; yield, 0.80 g. (quantitative). The combined product was recrystallized as just indicated, and gave thick rectangular plates that melted at 140°, as found by Goldschmidt and Ernst. Analysis (Kjeldahl) indicated the presence of only 1 acetyl radical.

Analysis. Subs., 0.3014: 18.10 cc. 0.1 N acid. Calc. for $C_9H_{11}O_2N$: N, 8.46 Found: 8.41.

o-Benzoyloxybenzyl-acetamide.—A compound having apparently this composition and structure was obtained by Auwers and Eisenlohr, 13 but they gave neither yield nor analysis of their product; the melting point they recorded is 108–109°; that found by us is 116°; yield, 93%.

Hydrolysis of the Acetyl-benzoyl Derivative.—A solution of 1.8 g. of the diacyl derivative just described, in 75 cc. of alcohol containing 0.85 g. (2.25 molecular equivalents) of potassium hydroxide, was allowed to stand for half an hour, after which it was made acid to congo red with hydrochloric acid. This caused the development of a pronounced odor of ethyl benzoate and a precipitation of potassium chloride. The salt was removed by filtration, the filtrate concentrated almost to dryness, and the residue

 $^{^{12}}$ Goldschmidt and Ernst tried to prepare this product by boiling the amine with acetic anhydride and anhydrous sodium acetate, but they obtained only the N-acetyl derivative and a small portion of an oily material having weak basic properties, which they assume may have been an anhydro base. We found that when a mixture of 1 part of base, 0.25 parts of dry sodium acetate and 4 parts of acetic anhydride, was treated as directed in our experiment described above, a yield of 74% of the diacetyl derivative was obtained.

¹³ Auwers and Eisenlohr, Ann., 369, 236 (1909).

then mixed with 25 cc. of water containing sufficient potassium hydroxide to bring about solution. After filtration, hydrochloric acid was added until a Sörensen value of 6–7 was reached, which caused the precipitation of 0.82 g. of solid. Removal of this and extraction of the mother liquor with chloroform gave 0.17 g. additional, a total of 0.99 g., which corresponds to a yield of 89.5% on the basis of the N-acetyl derivative as the product. The crude material melted at 135°, but purification by treatment of its chloroform solution with petroleum ether gave colorless irregular plates that melted at 140–141°. A mixture of this product and the N-acetyl derivative previously described melted at the same temperature as either of them separately.

o-Hydroxybenzyl-benzamide.—This compound was first obtained by treatment of 2.0 g. (2 molecular equivalents) of the free base suspended in 50 cc. of dry ether with 1 molecular proportion of benzoyl chloride dissolved in ether, according to Ransom's method. The product weighed 0.8 g., corresponding to a yield of only 43.4%. After solution in chloroform and precipitation by the addition of petroleum ether, it melted at $110-115^{\circ}$.

Recrystallization by treatment of a solution in absolute alcohol with petroleum ether gave short, thick needles that softened at 140° and melted at 142°. Further crystallization caused no change in melting point. The low yield here obtained made it advisable to find some other way to obtain this product, and this was done by hydrolysis of the dibenzoyl derivative (see below).

o-Benzoyloxybenzyl-benzamide.—To a solution of 3 g. of the free base in 300 cc. of water containing 2.1 molecular proportions of potassium hydroxide, was added 2.75 g. (2.15 molecular proportions) of benzoyl chloride, after which the material was shaken until the precipitation was complete; the liquid was still slightly acid to litmus. The solid, collected on a filter, washed and dried, weighed 8.5 g., which is more than the theoretical requirement. The excess may possibly be due to the formation of a tribenzoyl derivative. When the substance was purified by dissolving it in absolute alcohol and adding petroleum ether it separated in masses of long, thin needles that with the unaided eye had the appearance of paper pulp. It softened at 137° and melted to a clear liquid at 142–143°. Four recrystallizations caused no change in melting point. Analysis of an air-dried sample (Kjeldahl) indicated the presence of 2 benzoyl radicals.

Analysis. Subs., 0.6013: 18.02 cc. of 0.1 N acid. Calc. for $C_{21}H_{17}O_2N$: N, 4.23. Found: 4.20.

Preparation of o-Hydroxybenzyl-benzamide by Hydrolysis of the Dibenzoyl Derivative.—A solution of 3 g. of the dibenzoyl derivative just described in 150 cc. of alcohol containing 1.2 g. (2.25 molecular proportions) of potassium hydroxide was allowed to stand for 20 minutes, after which it was made acid to congo red by the addition of hydrochloric acid. The potassium chloride was removed and the filtrate evaporated under reduced pressure almost to dryness, after which 40 cc. of water was added, containing enough potassium hydroxide to dissolve the benzoyl derivative present. The mixture was filtered, and the ethyl benzoate removed by distillation in a vacuum. The remaining liquid was diluted to a volume of about 50 cc. and hydrochloric acid was added until a Sörensen value of 6–7 was reached. The precipitated benzoyl derivative was collected on a filter, washed and dried; yield, quantitative. It softened at 139° and melted to a clear liquid at 142–143°. After purification by solution in chloroform and the addition of petroleum ether, it was obtained in the form of rhombohedral plates that softened at 140° and melted sharply at 142°.

This material was shown not to be an impure sample of the dibenzoyl derivative

¹⁴ Ransom, Am. Chem. J., 23, 1 (1900).

¹⁵ Auwers and Eisenlohr, Ref. 13, p. 228, reported such a product from o-amino-p-cresol.

(m. p., 142-143°) from which it was prepared, by (a) the determination of the melting point of a mixture of the 2 products, found to be 110-115°; (b) by melting a mixture of the product here in question and the monobenzoyl compound obtained by Ransom's method (see above), in which case no depression was observed, and (c) by analysis for nitrogen, which indicated the presence of one benzoyl radical.

Analysis. Subs., 0.4013: 17.51 cc. of 0.1 N acid. Calc. for $C_{14}H_{15},O_2N$: N, 6.17. Found: 6.11.

Acetylation of the N-Benzoyl Derivative.—A mixture of $2.8~\rm g$. of the monobenzoyl compound, $0.75~\rm g$. of dry sodium acetate and $12~\rm g$. of acetic anhydride was gently boiled for $10~\rm minutes$. After the product had cooled, $50~\rm cc$. of water was added and the greater part of the acid and anhydride was neutralized by the addition of sodium bicarbonate. This caused crystals of the acetyl-benzoyl derivative to separate almost completely within a few minutes; yield $3.2~\rm g$., or $97~\rm \%$. The crude product softened at $70~\rm °$ and melted to a milky liquid at $80-83~\rm °$. Purification by solution in benzene and precipitation with petroleum ether gave irregular masses of poorly defined needles that softened at $80~\rm °$ and melted to a milky liquid at $85~\rm °$. Recrystallization from several other solvents caused no change in melting point. This product was further identified by analysis (Kjeldahl), which indicated the presence of both acetyl and benzoyl radicals.

Analysis. Subs., 0.5005: 18.42 cc. of 0.1 N acid. Calc. for $C_{16}H_{15}O_3N$: N, 5.20. Found: 5.17.

Finally, the melting point of a mixture of this material and the acetyl-benzoyl derivative (m. p., 116°) obtained by benzoylation of o-hydroxybenzyl-acetamide, was found to be 70–75°. This together with the analyses and the fact that these compounds give different products when hydrolyzed, indicates that they are isomeric and not identical, and that in the benzoylation of a phenol containing an acetylamino group attached to a side chain the migration characteristic of a derivative of o-aminophenol does not take place.

Hydrolysis of o-Acetyloxybenzyl-benzamide.—A solution of 1 g. of the product in 50 cc. of alcohol containing 0.47 g. (2.25 molecular proportions) of potassium hydroxide, was allowed to stand for 30 minutes. Hydrochloric acid was then added until the mixture reacted acid to congo red. The potassium chloride that had been precipitated was removed by filtration, and the filtrate concentrated under reduced pressure almost to dryness. The residue was washed from the flask with about 50 cc. of water and dried. The product weighed 0.7 g.; yield, 91%. It softened at 140° and melted at 142°. A mixture of this material and the N-benzoyl derivative prepared by the two methods indicated above showed no depression in melting point, while a mixture of this substance and the product (m. p., 140–141°) obtained by hydrolysis of o-benzoyloxybenzyl-acetamide melted at 110–120°.

Summary and Conclusions

- 1. An improvement of Nef's method for the preparation of sodium amalgam has been described.
- 2. It has been shown that, contrary to the results of Goldschmidt and Ernst, a very high yield of o-hydroxybenzylamine may be obtained by reduction of salicylaldoxime with sodium amalgam.
- 3. The observations here reported indicate that the migration of acyl previously shown to be characteristic of diacylated o-aminophenols does not occur when the amino radical is attached to a side chain.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PRODUCTION OF IMIDO THIOL ESTERS BY THE CONDENSATION OF THIOCYANATES WITH RESORCINOL OR PHLOROGLUCINOL

By R. J. Kaufmann with Roger Adams¹ Received February 12, 1923

The similarity in the reactivity of the cyano grouping in organic thiocyanates and cyanides is striking. The following table represents some of the commoner reactions of each which have already been described in the literature.

Reagent	Product with RCN	Product with RSCN
H_2	RCH_2NH_2	$RSH + CH_3NH_2^2$
H ₂ O (HCl)	RCONH ₂	$RSCONH_2$, $[RSC(=NH)(OH)]^3$
R'OH (HCl)	RC(=NH.HCI)OR'	$RSC(=NH.HCl)OR'^{4}$
H ₂ S	RCSNH ₂	$RSCSNH_2$, $[RSC(=NH)(SH)]^5$

In this communication is described the condensation of alkyl and aryl thiocyanates with resorcinol and phloroglucinol in the presence of hydrogen chloride and zinc chloride. This reaction corresponds to that studied by Hoesch in which alkyl and aryl cyanides are condensed with resorcinol and phloroglucinol under similar conditions. Whereas the cyanides yield imido hydrochlorides which hydrolyze to ketones, the thiocyanates readily yield imido thiol ester hydrochlorides, the expected products providing the cyano grouping in the thiocyanates react in the same way as the cyano in the cyanides. Methyl, ethyl, n-butyl and phenyl thiocyanates

HO OH RCN HO OH
$$C(=NH.HCl)R$$
 HO OH COR HO OH $C(=NH.HCl)SR$

were condensed with resorcinol, thus showing the reaction to be a general one. Only methyl thiocyanate was condensed with phloroglucinol, but

- ¹ This communication is an abstract of a thesis submitted by R. J. Kaufmann in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.
- ² Hofmann, Ber., 1, 177 (1868). Gerlich, Ann., 178, 82 (1875). Sestini and Funaro, Gazz. chim. ital., 12, 184 (1882). Fichter and Beck, Ber., 44, 3636 (1911).
- ³ (a) Salomon, J. prakt. chem., [2] 7, 256 (1873). (b) Conrad and Salomon, ibid.,
 [2] 10, 32 (1874). (c) Blankenhorn, ibid., [2] 16, 372 (1877). (d) Pinner, Ber., 14, 1082 (1881). (e) Knorr, ibid., 49, 1735 (1916).
 - 4 Ref. 3b.
- Jeanjean, Jahresber., 1866, 501. Ref. 3b, p. 29. Gerlich, Ann., 178, 82 (1875).
 Braun, Ber., 35, 3369, 3380 (1902). Bogert, This Journal, 25, 290 (1903). Delepine and Schving, Bull. soc. chim., [3] 29, 48 (1903); [4] 7, 895 (1910).

unquestionably the other thiocyanates would condense in an analogous way. The products thus obtained resembled in chemical reactivity known imido thiol ester hydrochlorides. Their exact constitution was proved by conversion into substances of known structure.

By the action of sodium bicarbonate these imido thiol ester hydrochlorides were decomposed into the free imido thiol esters. The latter substances, in contrast to many of this class of compounds previously described, were perfectly stable.⁶

The imido thiol ester hydrochlorides were readily decomposed into thiol esters by refluxing in very dilute aqueous hydrochloric acid solution. Since the thiol esters thus obtained were converted by alkali into the corresponding carboxylic acids which were made directly from resorcinol or phloroglucinol, the constitution of the original substances was definitely established.

The free imido thiol esters reacted readily with alcohols to give the corresponding imido esters and mercaptans. This is a reaction that is being investigated further. The imido esters obtained by this latter reaction were converted by hydrochloric acid to the corresponding salt and by boiling with dil. hydrochloric acid into the corresponding esters which, in the examples at hand, were known compounds and could readily be made by the esterification of the corresponding acids. The following chart gives in concise form the various reactions just discussed.

HO OH
$$C(=NH.HCl)SR$$
 HO OH $C(=NH)SR$ HO OH $C(=NH)OR'$

Boil with H_2O

HO OH $COSR$ HO OH $COSR$

The formation of the imido thiol ester hydrochlorides was very simple but there was some difficulty in their isolation on account of the zinc chloride used as a condensing agent. Washing with acetone removed a large amount of impurity from the crude condensation products but solution of the crude product in cold hydrochloric acid and reprecipitation of the base was necessary in order to eliminate completely the impurity of zinc. At least part of the zinc in the crude products was present not

⁶ Autenrieth and Brüning, Ber., 36, 3464 (1903). Bernthsen, Ann., 197, 341 ff, (1879).

merely as zinc chloride, but actually as a zinc salt of the phenol and in the condensation of the phenyl thiocyanate with resorcinol, it was actually possible to isolate and purify such a zinc compound. The initial condensations were also carried out without any zinc chloride, but under these conditions the reactions went much more slowly and did not yield so great an amount of the products. The materials obtained in this way, however, were always much purer.

Experimental Part

General Procedure for the Condensation of Alkyl and Aryl Thiocvanates with Resorcinol and Phloroglucinol.—A 1.5-liter wide-mouth bottle was equipped with a 3-hole rubber stopper through which were passed a mechanical stirrer with a mercury seal, an inlet tube with a wide mouth reaching to the bottom of the bottle, and an outlet tube which extended just through the stopper. To this outlet tube was attached a small upright water condenser, the upper end of which was closed with a tube leading through a sulfuric acid wash bottle. The moisture was thus prevented from returning to the reaction bottle and at the same time the speed with which the hydrogen chloride was flowing could be determined. In the bottle were placed 1 molecular equivalent each of phenol and thiocyanate, 0.2 to 1 molecular equivalent of pulverized anhydrous zinc chloride, and 250 to 1000 cc. of anhydrous ether. The stirrer was started and the mixture agitated for about 1 hour, until solution was complete. Dry hydrogen chloride was then bubbled into the solution for 30 to 40 hours, while rapid agitation was constantly maintained. Noticeable warming took place at the beginning and continued for 2 to 3 hours.

After 15 to 25 hours the separation of orange to deep red crystals began and continued for some time until complete. In some cases the reaction mixture at the end was semisolid, particularly when the smaller amounts of ether mentioned were used. The mixture was allowed to settle and the clear mother liquors decanted. The residue which was frequently sticky and dark colored, was extracted with cold acetone until a test portion imparted practically no further color to fresh solvent. The products thus obtained were light colored, granular solids.

It was advisable to return the mother liquors to the reaction bottle and again to pass in dry hydrogen chloride for some hours with vigorous stirring. In many cases an additional quantity of condensation product was thus obtained.

The further purification varied somewhat with the individual substances.

Methyl-thiol- β -resorcylate-imide Hydrochloride, (HO)₂C₆H₃C(\rightleftharpoons NH.HCl)SCH₃.—From 110 g. of resorcinol, 73 g. of methyl thiocyanate, 136 g. of zinc chloride and 275 cc. of anhydrous ether was obtained 130 to 160 g. of crude dry condensation product. In order to purify it from the zinc which it contained, it was crystallized twice from hot 15%

hydrochloric acid, washed with cold acetone and then dried at 100–110°. The product thus obtained was practically pure white and melted at 244–245° (corr.) decomp.

Analyses. Subs., 0.1340, 0.1944: AgCl, 0.0886, 0.1289. Subs., 0.1963, 0.2242: BaSO₄, 0.2085, 0.2399. Subs., 0.2190, 0.2042: 5.290, 5.041 cc. of 0.1930 N HCl. Calc. for $C_8H_{10}O_2CINS$: Cl, 16.15; S, 14.60; N, 6.38. Found: Cl, 16.36, 16.40; S, 14.59, 14.69; N, 6.53, 6.67.

Methyl-thiol- β -resorcylate-imide Sulfate, (HO)₂C₆H₃C (=NH. $\frac{1}{2}$ H₂SO₄)SCH₃.—A solution of 5 g. of the crude hydrochloride in 10 cc. of water was filtered and the filtrate treated with 10 cc. of 50% (by volume) sulfuric acid. After 24 hours, crystals of the sulfate separated. These were recrystallized once from 25% (by weight) sulfuric acid, then from alcohol and finally washed with dry ether. The product formed white crystals; m. p., 230–231.5° (corr.).

Analyses. Subs., 0.2305, 0.2339; 4.951, 5.071 cc. of 0.1917 N HCl. Calc. for $C_{16}H_{20}O_8N_2S_3$: N, 6.03. Found: 5.77, 5.82.

Ethyl-thiol- β -resorcylate-imide Hydrochloride, (HO)₂C₆H₃C(=NH.HCl)SC₂H₅.— From 110 g. of resorcinol, 87 g. of ethyl thiocyanate, 136 g. of zinc chloride and 275 cc. of ether was obtained 140–160 g. of crude solid. This product tended to remain pink even after action of the acetone. The color could be removed, however, by dissolving the product in ice water and adding coned. hydrochloric acid. The cream-colored product was then recrystallized from 15% hydrochloric acid and, after it had dried, melted at 229.5–231.5° (corr.) decomp.

Analyses. Subs., 0.3452, 0.3499; 7.534, 7.627 cc. of 0.1930 N HCl. Calc. for $C_0H_{12}O_2NCIS$: N, 6.00. Found: 5.90, 5.89.

Ethyl-thiol- β -resorcylate-imide Sulfate, (HO)₂C₆H₃C(=NH. $\frac{1}{2}$ H₂SO₄)SC₂H₅.—The method of preparation was similar to that of the corresponding methyl compound. The substance was purified by crystallization from 95% alcohol or glacial acetic acid. It formed a white powder; m. p., 214–217° (corr.).

Analyses. Subs., 0.2112, 0.4461; 4.285, 8.870 cc. of 0.1930 N HCl. Calc. for $C_{18}H_{24}O_8N_2S_3$: N, 5.69. Found: 5.49, 5.38.

n-Butyl-thiol-β-resorcylate-imide Hydrochloride, (HO)₂C₆H₃C(\rightleftharpoons NH.HCl)SC₄H₉ (n).—The butyl derivative was readily obtained from resorcinol, n-butyl thiocyanate,⁷ zinc chloride and anhydrous ether. It was purified by crystallization from a mixture of equal volumes of 95% alcohol and 15% hydrochloric acid. When pure the substance was white and melted at 226–228° (corr.) decomp.

Analyses. Subs., 0.1591, 0.1146: AgCl, 0.0865, 0.0608. Subs., 0.2083, 0.1265: BaSO₄, 0.1856, 0.1115. Subs., 0.3332, 0.4236; 6.701, 8.218 cc. of 0.1930 N HCl. Calc. for $C_{11}H_{16}O_2NSCl$: CI, 13.55; S, 12.26; N, 5.35. Found: Cl, 13.45, 13.13; S, 12.24, 12.11; N, 5.44, 5.25.

Phenyl-thiol- β -resorcylate-imide Hydrochloride, $(HO)_2C_6H_3C$ (=NH.HCl)SC $_6H_5$. —From 22 g. of resorcinol, 27 g. of phenyl thiocyanate, 5 g. of zinc chloride and 250 cc. of anhydrous ether was obtained 12 g. of crude product. When this substance was crystallized from approximately 2% aqueous hydrochloric acid, a white product was formed. This was crystallized further by dissolving in the smallest amount of alcohol

 $^{^7}$ n-Butyl thiocyanate has not been described in the literature. It was made by the general procedure described in Ann., 178, 85 (1882) from n-butyl bromide and ammonium thiocyanate; yield, 85–90%. The product had the following constants: b. p., 744 mm. 184.5–185.5°; d_*^{25} , 0.9563; $n_D^{21.5}$, 1.4636.

Analysis. Subs., 0.3369, 0.3084: 14.940, 13.959 cc. of 0.1917 N HCl. Calc. for C_5H_9NS : N, 12.17. Found: 11.91, 12.16.

possible and gradually precipitating with dry ether in the cold. The substance was then pure and white, and melted at 220–222° (corr.) decomp.

Analysis. Subs., 0.1511, 0.1533: BaSO₄, 0.1228, 0.1252. Subs., 0.0950, 0.3681: 1.771, 6.850 cc. of 0.1892 N HCl. Calc. for $C_{13}H_{12}O_2NCIS$: S, 11.38; N, 4.98. Found: S, 11.16, 11.22; N, 4.95, 4.93.

The crude material was apparently a fairly pure zinc salt of the condensation product. The zinc salt was prepared for analysis by dissolving the acetone-washed substance, in 10 times its weight of cold 95% alcohol, filtering the solution and adding an equal volume of concd. hydrochloric acid. The substance then separated in the form of small, light-yellow crystals which were finally washed with acetone. Repetition of this treatment did not raise the melting point, which was $225-227^{\circ}$ (corr.) decomp.

Analysis. Subs., 0.1711, 0.1663; BaSO₄, 0.1105, 0.1099. Subs., 0.2517, 0.2756; 3.769, 4.202 cc. of 0.1892 N HCl. Calc. for $C_{13}H_{10}O_2NClSZn$: S, 9.29; N, 4.06. Found: S, 8.87, 9.08; N, 3.97, 4.04.

Methyl-thiol-2,4,6-trihydroxy-benzoate-imide Hydrochloride, (HO) $_3$ C $_6$ H $_2$ C(:=NH. HCl)SCH $_3$.—From 35 g. of phloroglucinol, 21 g. of methyl thiocyanate, 7 g. of zinc chloride and 250 cc. of anhydrous ether, was obtained after about 20 hours 22 g. of crude product. When the filtrate was treated for another 10–15 hours with dry hydrogen chloride, an additional 14.3 g. of crude product was formed. It was purified by dissolving it in a hot mixture of 2 parts by volume of alcohol and 3 parts of 15% hydrochloric acid, boiling the mixture with charcoal, filtering and cooling the filtrate. The product was white when pure and melted at 255–256° (corr.).

Analyses. Subs., 0.2299, 0.3698; 4.842, 8.000 cc. of 0.1892 N HCl. Calc. for C_8H_{10} -O₃NClS; N, 5.95. Found: N, 5.58, 5.73.

General Procedure for Conversion of the Imido Thiol Ester Hydrochlorides to Imido Thiol Esters.—The pure imido thiol ester hydrochlorides were dissolved in 3 to 5 times their weight of water, the solutions cooled and sufficient saturated sodium bicarbonate solution was added to make the mixtures alkaline. The bases which precipitated were filtered, and washed with water.

When the crude imido thiol ester hydrochlorides which contained zinc were converted into the free bases, it was necessary to add only enough sodium bicarbonate in the precipitation to leave the mixture just acid to litmus. The major portion of the zinc thus remained in solution. The bases were filtered, dissolved again in the minimum amount of dil. hydrochloric acid, and again precipitated as just described. In this way bases entirely free from zinc salts were obtained.

Methyl-thiol- β -resorcylate-imide, (HO)₂C₆H₃C(=NH)SCH₃.—For complete purification, this substance was crystallized from hot methyl alcohol. This must be done rapidly since methyl alcohol gradually reacts with the compound. When pure, the substance was obtained in the form of small yellow needles; m. p., 197–199° (corr.) decomp.

Analyses. Subs., 0.1397, 0.1115: BaSO₄, 0.1744, 0.1409. Subs., 0.1585, 0.2298: 4.394, 6.710 cc. of 0.1930 N HCl. Calc. for C₈H₉O₂NS: S, 17.50; N, 7.65. Found: S, 17.14, 17.35; N, 7.50, 7.90.

Ethyl-thiol- β -resorcylate-imide, (HO)₂C₅H₃C(\Longrightarrow NH)SC₂H₅.—This product was crystallized from ethyl alcohol from which it formed yellow crystals; m. p., 196–197°

(corr.) decomp. It was not allowed to stand with the ethyl alcohol since these substances gradually reacted.

Analyses. Subs., 0.2482, 0.2814: 6.383, 7.378 cc. of 0.1930 N HCl. Calc. for $C_9H_{11}O_2NS$: N, 7.11. Found: 6.95, 7.09.

n-Butyl-thiol- β -resorcylate-imide, (HO) $_2$ C $_6$ H $_3$ C(\Longrightarrow NH)SC $_4$ H $_9$ (n).—This substance was finally purified by crystallization from methyl alcohol. It was not allowed to stand with the methyl alcohol since the 2 substances gradually reacted. Bright yellow needles were formed; m. p., 173–174° (corr.) decomp.

Analyses. Subs., 0.1626, 0.1613: BaSO₄, 0.1661, 0.1630. Subs., 0.3710, 0.4816; 8.575, 10.860 cc. of 0.1930 N HCl. Calc. for $C_{11}H_{15}O_2NS$: S, 14.24; N, 6.22. Found: S, 14.03, 13.88; N, 6.25, 6.10.

Phenyl-thiol- β -resorcylate-imide, $(HO)_2C_6H_3C(\rightleftharpoons NH)SC_6H_5$.—The base was crystallized by solution in alcohol and precipitation with water or by partial evaporation of an alcohol-ether solution. The compound formed yellow crystals which, after they were dried at 80°, melted at 156–158° (corr.) decomp.

Analyses. Subs., 0.1882, 0.1568: 3.880, 3.340 cc. of 0.1892 N HCl. Calc. for $C_{13}H_{11}O_{2}NS$: N, 5.72. Found: 5.47, 5.65.

Methyl-thiol-2,4,6-trihydroxy-benzoate-imide, $(HO)_5C_6H_2C(=NH)SCH_3$.—This substance proved to be very much less soluble in the common organic solvents than any of the other imido thiol esters studied. No satisfactory solvent was found. The base was made from very pure hydrochloride and prepared for analysis by washing with boiling water, boiling alcohol, and absolute ether, giving then a cream colored product; m. p., 223–226° (corr.).

Analyses. Subs., 0.1386, 0.2258: BaSO₄, 0.1586, 0.2632. Subs., 0.2150, 0.3040: 5.331, 7.601 ee. of 0.1917 N HCl. Cale. for $C_8H_9O_5NS$: S, 16.10; N, 7.04. Found: S, 15.71, 16.01; N, 6.66, 6.72.

General Procedure for the Formation of Thiol Esters from the Imido Thiol Ester Hydrochlorides.—Pure imido thiol ester hydrochloride was dissolved in very dilute hydrochloric acid and refluxed for 2 to 5 hours in the case of the resorcinol derivatives, or 8 to 10 hours in the case of phloroglucinol derivatives which were more difficult to hydrolyze. Solid products, which separated as the solutions cooled, were filtered directly; liquids were extracted with ether.

Methyl-thiol-β-resorcylate-monohydrate, (HO)₂C₆H₃COSCH₃.H₂O.—From 35 g. of once recrystallized methyl-thiol-β-resorcylate-imide hydrochloride in 1500 cc. of water and 5 cc. of coned. hydrochloric acid was obtained after 5 hours 25 g. of product which, solidified as the reaction mixture cooled. This was purified by solution in a little boiling alcohol to which bone charcoal was added, filtration and reprecipitation with water. Finally, it was recrystallized from 50% alcohol, as colorless needles; m. p., 70–71° (corr.).

Analyses. Subs., 0.1424, 0.1510: BaSO₄, 0.1625, 0.1699. Subs., 0.9051: H_2O , 0.0823. Calc. for $C_8H_8O_8S.H_2O$: S, 15.87; H_2O , 8.92. Found: S, 15.67, 15.45; H_2O , 9.09.

The monohydrate was readily converted to the anhydrous ester by drying it in a vacuum desiccator or by warming it first at 55° and later at 70° for 4–6 hours. The anhydrous ester was recrystallized from benzene or chloroform, and when pure melted at 97–98° (corr.).

Analyses. Subs., 0.1447, 0.1409: BaSO₄, 0.1833, 0.1762. Calc. for C₈H₈O₈S: S, 17.41. Found: 17.40, 17.17.

Bis(p-nitrobenzoyl)-methyl-thiol- β -resorcylate, ((p)NO₂C₆H₄CO₂)₂C₆H₃COCSH₃.—Three g. of methyl-thiol- β -resorcylate in 40 cc. of 10% sodium hydroxide solution was shaken with 11.1 g. of pulverized p-nitrobenzoyl chloride and the shaking continued until heat was no longer evolved and the acid chloride had disappeared. The precipitate was filtered, washed with water, extracted with boiling alcohol and finally recrystallized from ethyl acetate as colorless crystals; m. p., 214–216° (corr.).

Analyses. Subs., 0.1203, 0.1176: BaSO₄, 0.0597, 0.0570. Subs., 0.1351, 0.3062: 2.881, 6.399 cc. of 0.1930 N HCl. Calc. for $C_{22}H_{14}O_{9}N_{2}S$: S, 6.65; N, 5.81. Found: S, 6.81, 6.66; N, 5.77, 5.65.

Ethyl-thiol- β -resorcylate, $(HO)_2C_6H_3COSC_2H_5$.—Five g. of pure imide hydrochloride in 200 cc. of water and 5 cc. of 15% hydrochloric acid, refluxed for 2 hours, gave a reddish oil. This was extracted with ether and the solution washed with dil. hydrochloric acid, then dil. sodium bicarbonate and finally with water. The ether solution was placed in a vacuum desiccator over sulfuric acid. The ether was evaporated and an oil was left which gradually solidified. It was a substance difficult to purify. The crude product was dissolved in a little ether, and a little petroleum ether added to precipitate the colored material, the solution filtered, evaporated in a vacuum desiccator over sulfuric acid, and the residual oil inoculated with a crystal of thiol ester. After two such treatments, white crystals were obtained melting at 60–61°.

Analyses. Subs., 0.1614, 0.1241: BaSO₄, 0.1846, 0.1410. Calc. for $C_9H_{10}O_9S$: S, 16.18. Found: 15.71, 15.60.

Bis(p-nitrobenzoyl)-ethyl-thiol- β -resorcylate, $((p)NO_2C_6H_4CO_2)_2C_6H_3COSC_2H_5$.—This substance was made by the method described for the methyl derivative. The product was crystallized from ethyl acetate as white crystals; m. p., 190–191° (corr.).

Analyses. Subs., 0.1962, 0.2413: 4.210, 5.190 cc. of 0.1917 N HCl. Calc. for $C_{28}H_{15}O_{9}N_{2}S$: N, 5.65. Found: 5.76, 5.78.

n-Butyl-thiol- β -resorcylate, $(HO)_2C_6H_3COSC_4H_9(n)$.—After refluxing 13 g. of pure n-butyl-thiol- β -resorcylate-imide hydrochloride in 200 cc. of water for 2–3 hours, thiol ester was obtained in the form of a light brown oil. To obtain this as a solid was impossible and consequently purification was difficult. For identification it was converted into the bis-p-nitrobenzoate.

Bis(p-nitrobenzoyl)n-butyl-thiol- β -resorcylate, $((p)\mathrm{NO}_2\mathrm{C}_6\mathrm{H}_4\mathrm{CO}_2)_2\mathrm{C}_6\mathrm{H}_3\mathrm{COSC}_4\mathrm{H}_9$ -(n).—Upon treatment of this oil with p-nitrobenzoyl chloride as described for the methyl ester, a solid product was obtained. This was extracted twice with boiling alcohol, then recrystallized from ethyl acetate. When pure it was a colorless compound; m. p., 115–116° (corr.).

Analyses. Subs., 0.1555, 0.1200: BaSO₄, 0.0657, 0.0561. Subs., 0.2968, 0.2819; $^\circ$ 6.073, 5.518 cc. of 0.1930 N HCl. Calc. for $C_{26}H_{20}O_9N_2S$: S, 6.12, N, 5.35. Found: S, 5.80, 6.42; N, 5.53, 5.29.

Methyl-thiol-2,4,6-trihydroxy-benzoate, $(HO)_3C_6H_2COSCH_3$.—A solution of 3.5 g. of pure methyl-thiol-2,4,6-trihydroxy-benzoate-imide hydrochloride in 250 cc. of water and 15 cc. of 15% hydrochloric acid was refluxed for 8 to 10 hours, cooled and extracted with ether. A pink solid was obtained which was purified by recrystallization from 10% alcohol. After drying at $100-110^\circ$ the product was white and melted at 190° (corr.).

Analyses. Subs., 0.1474, 0.1142: BaSO₄, 0.1735, 0.1341. Calc. for C₈H₈O₄S: S. 16.02. Found: 16.16, 16.13.

Methyl- β -resorcylate-imide, (HO)₂C₆H₃C(\rightleftharpoons NH)OCH₃.—A mixture of 200 cc. of absolute methyl alcohol and 7 g. of methyl-thiol- β -resorcylate-imide was refluxed for 2 hours. The alcohol was then distilled, leaving a reddish-brown solid. This was recrystallized from methyl alcohol, giving white needles; m. p., 210° (corr.).

Analyses. Subs., 0.1648, 0.1809: 5.026, 5.643 cc. of 0.1930 N HCl. Calc. for $C_8H_9O_8N$: N, 8.39. Found: 8.25, 8.44.

This base was converted into the corresponding hydrochloride by saturation of a small amount of a hot 15% hydrochloric acid solution with the free imide ester and filtration. The crystals, formed as the solution cooled, were purified by recrystallization from 15% hydrochloric acid, and the purified product melted at 166–168° and was presumably a hydrate, since upon drying in a vacuum desiccator the melting point changed to 224–226° (corr.) where it remained constant.

Analyses. Subs., 0.2585, 0.2182: 6.399, 5.415 cc. of 0.1930 N HCl. Calc. for $C_8H_{10}O_3NCl$: N, 6.88. Found: 6.70, 6.71.

n-Butyl-thiol- β -resorcylate-imide also was readily converted into the methyl- β -resorcylate-imide in the same way. After a mixture of 5 g. of pure n-butyl-thiol- β -resorcylate-imide and 50 cc. of absolute methyl alcohol was refluxed for about 1 hour a homogeneous solution formed and in another hour colorless crystals began to appear. The refluxing was continued for 2–3 hours longer and then the mixture was allowed to stand overnight. The product was filtered and more crystals were obtained by dilution of the filtrate. The material was purified from methyl alcohol after which it melted at 210° (corr.). This material was also converted into the hydrochloride which corresponded exactly to the one described just above.

Ethyl- β -resorcylate-imide, (HO)₂C₆H₃C(\rightleftharpoons NH)OC₂H₅.—A mixture of 5 g. of pure ethyl-thiol- β -resorcylate-imide and 100 cc. of absolute ethyl alcohol was refluxed for 5 hours and then cooled when crystals separated. These were removed and from the filtrate more were recovered by evaporation of the alcohol. The product was purified by crystallization from ethyl alcohol; m. p., 214° (corr.).

Analyses. Subs., 0.2301, 0.1681: 6.461, 4.896 cc. of 0.1930 N HCl. Calc. for $C_9H_{11}O_3N$: N, 7.74. Found: 7.59, 7.88.

Methyl- β -resorcylate from Methyl- β -resorcylate-imide, (HO)₂C₆H₃CO₂CH₃.—A suspension of 0.5 g. of methyl- β -resorcylate-imide in 20 cc. of water, treated with just enough dil. hydrochloric acid to cause complete solution, was refluxed for 2 hours and then cooled, whereupon white crystals separated. These were filtered, washed with a little cold water and crystallized from benzene or a little 50% alcohol. After crystallization they melted at 116–117° (corr.) and proved to be identical with methyl- β -resorcylate made by esterification of β -resorcylate-imide hydrochloride with water.

Ethyl- β -resorcylate from Ethyl- β -resorcylate-imide (HO)₂C₆H₃CO₂C₂H₅.—A solution of 0.75 g. of ethyl- β -resorcylate-imide in 30 cc. of water and 1 cc. of 15% hydrochloric acid was refluxed for about 1 hour. Hydrolysis took place and ethyl- β -resorcylate separated as an oil. This was cooled with ice until it solidified, and the solid was filtered and recrystallized from water. After drying for 36 hours in a desiccator it melted at 69–70° (corr.). The same product was obtained also from β -resorcylic acid by refluxing it for 10 hours with absolute alcohol saturated with dry hydrogen chloride. The alcohol was then distilled, the residue washed with dil. sodium bicarbonate solution, and the red oil which resulted was distilled under diminished pressure (b. p., 13–15 mm., 170–176°). The distillate solidified and was purified further by crystallization from water. After drying, it melted at 69–70° and proved to be identical with the product described above.

Analysis. Subs., 0.2605: 331 cc. of CO₂ (25°, 742.5 mm.). Calc. for $C_9H_{10}O_4$: C, 59.31. Found: 59.00.

 β -Resorcylic Acid from Methyl-thiol- β -resorcylate.—A solution of 10 g. of methyl-thiol- β -resorcylate in 100 cc. of 10% potassium hydroxide solution was heated on a water-

⁸ Baeyer, Ann., 372, 85 (1910).

bath at about 70° for 30 hours, cooled and acidified just to the point at which congo red paper changed color, when a precipitate of β -resorcylic acid formed. The solution and precipitate were extracted a few times with ether, and the β -resorcylic acid again obtained in an aqueous solution by shaking the ether extract with a solution of sodium bicarbonate. The aqueous solution was neutralized as before, the free acid extracted with ether, and the ether solution dried and then evaporated. About 4 g. of solid was thus obtained which was crystallized once from water and bone charcoal and once from water. White crystals resulted which after drying melted at 215–217° with evolution of carbon dioxide. A mixed melting point with resorcylic acid® made in the usual way gave no depression.

Summary

- 1. Alkyl and aryl thiocyanates, as represented by methyl, ethyl, n-butyl and phenyl thiocyanates, were condensed with resorcinol and phloroglucinol in the presence of anhydrous ether, dry hydrogen chloride and anhydrous zinc chloride. The products which were obtained were imido thiol ester hydrochlorides.
- 2. These substances, upon treatment with sodium bicarbonate, were converted into the imido thiol esters.
- 3. The imido thiol ester hydrochlorides, refluxed in aqueous solution, were hydrolyzed to thiol esters. These substances, upon saponification, yielded compounds containing a carboxyl group.
- 4. The imido thiol esters, upon treatment with alcohols as represented by the formula R'OH, were converted upon long standing or refluxing into the corresponding imido esters. These oxygen imido esters, upon treatment with acids, yielded the corresponding salts, or when boiled with acids were decomposed into the corresponding carboxylic esters.
- 5. From these results it is obvious that the cyanogen group in thiocyanates acts similarly to the cyanogen group in alkyl cyanides when treated with certain types of phenols, hydrogen chloride and anhydrous zinc chloride.

URBANA, ILLINOIS

⁹ Kostanecki, Ber., 18, 1985 (1885). Nierenstein, J. Chem. Soc., 107, 1494 (1915).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

SOME MERCURY DERIVATIVES OF PHENOL ETHERS1

By Frank C. Whitmore and Edmund Burrus Middleton²
Received February 23, 1923

In an earlier paper³ it was shown that mercurated phenols react with iodides of alkali metals to give the original phenols, inorganic mercury compounds and 1 equivalent of alkali for each carbon-mercury linkage broken. When, however, the hydroxyl group is protected by acylation iodides react in quite a different way giving mercuri-bis compounds and inorganic mercury compounds but not alkali. The two processes may be illustrated as follows.

$$\begin{array}{c} \text{HO---}C_6H_4\text{---}HgI + 3 \text{ KI} + H_2O \longrightarrow C_6H_6OH + K_2HgI_4 + KOH} \\ \text{2 AcO---}C_6H_4\text{---}HgI + 2 \text{ KI} \longrightarrow (AcO---C_6H_4)_2Hg + K_2HgI_4 \end{array}$$

The present work was undertaken to determine the effect of replacing the phenolic hydrogen by an alkyl group instead of an acyl group. An observation made by Dimroth⁴ indicated that the effect of the 2 groups might be similar. In determining the structure of o-chloromercuri-phenol, he treated it with ethyl iodide in alkaline alcoholic solution to prepare the known o-phenetylmercuric iodide. Besides the desired product he obtained a good yield of o-mercury-diphenetyl. Since sodium iodide is formed in the reaction it seemed reasonable that it might change the mercurated phenetole first formed to the mercuri-bis compound. Dimroth's results may then be formulated as follows.

$$\begin{array}{c} NaO-C_6H_4-HgCl+RI \longrightarrow RO-C_6H_4-HgCl+NaI\\ 2\;RO-C_6H_4-HgCl+4\;NaI \longrightarrow (RO-C_6H_4)_2Hg+Na_2HgI_4+2\;NaCl \end{array}$$

In order to test this theory and to study further the effect of protecting a phenolic hydroxyl group upon the stability of the carbon-mercury linkage, the action of potassium iodide on mercurated phenol ethers was studied.

Iodomercuri-anisoles and -phenetoles were prepared by the method of Dimroth.⁴ As the *ortho* mercurated compounds are much more soluble than the *para* compounds, the study was limited to the former. When an alcoholic solution of *o*-iodomercuri-anisole or of *o*-iodomercuri-phenetole is refluxed with potassium iodide, no splitting of the carbon-mercury linkage takes place as no alkali is formed. *o*-Mercury-dianisyl or *o*-mercury-diphenetyl is obtained in good yield. The mother liquors contain large amounts of inorganic mercury compounds. Potassium thiocyanate acts

- ¹ Presented at the Rochester Meeting of the American Chemical Society, April, 1921.
- ² Research Fellow under a grant from the U. S. Interdepartmental Social Hygiene Board, General M. W. Ireland, Chairman. Some of the organic mercury compounds related to those studied are being investigated pharmacologically under the direction of Dr. A. S. Loevenhart of the Department of Pharmacology of the University of Wisconsin.
 - ³ This Journal, 43, 622 (1921).
 - 4 Dimroth, Ber., 32, 763 (1899).

like potassium iodide but gives poorer yields of the mercuri-bis compounds.

The para mercurated phenol ethers react to some extent with potassium iodide or with potassium thiocyanate; some inorganic mercury is formed. No alkali is found. The corresponding mercuri-bis compounds are not obtainable in a pure state by these reactions.

Sodium thiosulfate is the most convenient reagent for making the mercuri-bis compounds of the phenol ethers. The *o*-iodomercuri compounds dissolve readily in it giving solutions from which the mercuri-bis compounds separate on standing.

o-Mercury-dianisyl and o-mercury-diphenetyl react normally with mercuric chloride; quantitative yields of the chloromercuri compounds are obtained.

Experimental Part

Preparation of o- and p-Iodomercuri-phenetoles.—A mixture of 5 g. of o-chloromercuri-phenol³ in 50 cc. of 50% ethyl alcohol, 0.7 g. of sodium hydroxide, and 3.5 g. of ethyl iodide is heated gently for 1 hour. A small amount of o-mercury-diphenetyl separates as the solution cools. This is removed and the filtrate is diluted with water to precipitate the o-iodomercuri-phenetole which is recrystallized from alcohol; yield, 7 g. The para compound is prepared in a similar way. Five g. of p-chloromercuri-phenol gives 5 g. of a mixture of the corresponding iodomercuri and mercuri-bis-compounds which is difficult to separate. Because the ortho compounds are obtained more easily, the experiments with potassium iodide, with thiocyanate, and with thiosulfate were carried out with o-iodomercuri-phenetole and o-iodomercuri-anisole.

Preparation of o-Iodomercuri-anisole.—Eight g. of o-chloromercuri-phenol, 1 g. of sodium hydroxide, 50 cc. of alcohol, and 3 g. of methyl iodide are heated for half an hour. About 1 g. of o-mercury-dianisyl separates as the solution cools. Dilution of the mother liquor with water gives 7 g. of the iodomercuri compound.

Reaction of Potassium Iodide with o-Iodomercuri-anisole and with o-Iodomercuri-phenetole.—Four g. of o-iodomercuri-anisole, recrystallized from alcohol, is heated under a reflux condenser for 6 hours with 3 g. of potassium iodide and 50 cc. of alcohol. When the product is cooled and diluted somewhat the o-mercury-dianisyl is precipitated. It is recrystallized from alcohol; yield, 1.5 g.; m. p., 108°. The filtrate from the reaction mixture is neutral and gives an immediate precipitate with hydrogen sulfide.

A solution of 2 g. of o-iodomercuri-phenetole in 50 cc. of alcohol together with 2 g. of potassium iodide is refluxed for 1 hour. When this product is cooled and diluted with water, 1.5 g. of o-mercury-diphenetyl separates. After crystallization from alcohol it melts at 81°. The filtrate is not alkaline. It contains inorganic mercury compounds.

Reaction of Potassium Thiocyanate with the o-Iodomercuri-phenol Ethers.—A mixture of 2 g. of o-iodomercuri-anisole, 2 g. of potassium thiocyanate and 50 cc. of alcohol was heated under a reflux condenser for 3 hours. The product, cooled and diluted, gave 1.5 g. of the mercuri-bis compound. Recrystallization from alcohol raised the melting point only to 75–80°. The filtrate contains inorganic mercury compounds but is neutral.

A mixture of 1.6 g. of o-iodomercuri-phenetole, 2 g. of potassium iodide and 50 cc. of alcohol, heated under a reflux condenser for 3 hours gives 0.8 g. of the mercuri-bis compound melting at 80° after several crystallizations from alcohol.

Reaction of Sodium Thiosulfate with the o-Iodomercuri-phenol ethers.—Two g. of o-iodomercuri-phenetole dissolved in a solution of 4 g. of sodium thiosulfate in 50 cc. of water deposits 1.2 g. of the mercuri-bis compound on standing; m. p., 81–83°.

Similarly, o-iodomercuri-anisole gives the mercuri-bis compound melting at 108° .

Reaction of the p-Iodomercuri-phenol Ethers with Potassium Iodide and with Potassium Thiocyanate.—The reactions between these substances apparently lead to the formation of mercuri-bis compounds, as the filtrates contain inorganic mercury and are not alkaline. However, the products are very difficult to purify.

Reaction of Mercuric Chloride with the Mercuri-bis-phenol Ethers.—One g. of o-mercury-dianisyl is heated with 0.7 g. of mercuric chloride in 25 cc. of alcohol for 15 minutes. The chloride deposits on cooling, and is recrystallized from alcohol; m. p., $177-178^\circ$. Dimroth obtained the same compound in small amount by direct mercuration of anisole. He gives the melting point as $173-174^\circ$.

Similarly, o-mercury-diphenetyl reacts with mercuric chloride to give pure o-chloromercuri-phenetole.

Summary

- 1. Protection of the hydroxyl groups in mercurated phenols by alkylation has the same effect as protection by acylation, that is, the stability of the carbon-mercury linkage to iodides, thiocyanates, and to thiosulfates is increased.
- 2. Mercurated phenol ethers react with iodides, with thiocyanates, and with thiosulfates to form the corresponding mercuri-bis compounds giving solutions which contain inorganic mercury but no alkali, showing that the protection of the phenolic hydroxyl has prevented the splitting of the carbon-mercury linkage with the accompanying formation of alkali which occurs with the mercurated phenols.
- 3. The formation of the mercuri-bis compounds takes place much more readily in the case of the *ortho* compounds than with the *para* compounds.

EVANSTON, ILLINOIS

[Contribution from the Research Laboratory of the Eastman Kodak Company, No. 174]

THE PREPARATION OF ALKYLGUANIDINES

By Ross Phillips and H. T. Clarke Received February 24, 1923

In a recent paper, Arndt¹ describes a new and convenient reagent, methyl iso-thio-urea sulfate, from which methyl mercaptan may be obtained in a pure condition by warming it with dil. alkalies; dicyanodiamide is formed as a by-product. This reagent, produced by the addition of dimethyl sulfate to thio-urea, bears a close relation to the alkyl iodide addition products of thio-urea,² which react with primary and secondary aliphatic amines to form alkyl guanidines and alkyl mercaptans.

We have found that methyl iso-thio-urea sulfate undergoes an exactly analogous reaction with methylamine and dimethylamine, methyl mercap-

¹ Arndt, Ber., 54B, 2236 (1921).

² Wheeler and Jamieson, J. Biol. Chem., 4, 111 (1907). Schenck, Z. Physiol. Chem., 77, 328 (1912).

tan and methylguanidine sulfate (and α , α -dimethylguanidine sulfate) being produced in excellent yield, without the use of an appreciable excess of the base. As far as we can ascertain, these sulfates have hitherto never been described; they crystallize well from water and are practically insoluble in methyl alcohol. The reaction does not take place with aniline, either alone or in the presence of alkali.

Incidentally to the isolation of the methyl mercaptan, which is formed as a by-product, we have found that when the gas is passed into a 25% solution of sodium hydroxide the sodium salt of methyl mercaptan crystallizes in long, flat needles of the composition, $2CH_3SNa.9H_2O$.

Experimental Part

Methylguanidine Sulfate.—To a suspension of 700 g. of methyl iso-thio-urea sulfate in 700 cc. of cold water is added, all at once, 525 g. of a 33% aqueous solution of methylamine. The vessel is immediately fitted with a reflux condenser, from the upper end of which tubes lead the evolved gas through a wash bottle containing 250 cc. of 10% hydrochloric acid (to remove any entrained methylamine) into 700 cc. of a 25% solution of sodium hydroxide cooled by running water. When the mixture in the flask is shaken and gently warmed, a vigorous reaction sets in at about 30°; methyl mercaptan is evolved at a steady rate without application of heat. When the reaction slackens, the mixture is heated until finally it boils; it is then concentrated under reduced pressure until the weight is about 1000 g. The resulting sirup is chilled to —5°, whereupon it sets to a mass of crystals; 300 cc. of methyl alcohol is then added and the crystals are collected by suction and washed with cold methyl alcohol in which the product is practically insoluble. The yield of pure dry methylguanidine sulfate is about 500 g., or 82%; m. p., 239–240°.

Analysis. Subs., dried at 120°, 0.4826: BaSO₄, 0.4675. Calc. for $C_4H_{16}O_4N_6S$: S, 13.12. Found: 13.30.

The combined filtrates and washings are concentrated to 300 g., cooled to 50°, and treated with 60 cc. of nitric acid (d., 1.42). The mixture is chilled to 0° and the resulting crystals of the nitrate are collected: when dry, this material weighs about 90 g., a 13% yield. After recrystallization from rather less than its own weight of water, it melts at 149–150°.

The picrate 3 (prepared both from the sulfate and from the nitrate) melts at 199–200 $^{\circ}.^4$

 α, α -Dimethylguanidine Sulfate.—A suspension of 250 g. of methyl iso-thio-urea sulfate in 300 cc. of cold water is treated exactly as above with 285 g. of a 33% aqueous solution of dimethylamine. After the reaction is complete, the solution is concentrated under reduced pressure until crystals begin to form, chilled to 0°, and the crystals are collected on a filter and washed with methyl alcohol. The mother liquors are again concentrated, and the recrystallization process is repeated twice. In this way 200 g. of α, α -dimethylguanidine sulfate, melting with decomposition at 285–288°, is obtained, an 82% yield.

Analysis. Subs., dried at 120°, 0.4581: BaSO₄, 0.4052. Calc. for $C_6H_{18}O_4N_6S$: S, 12.40. Found: 12.13.

³ Fischer, Ber., 30, 2414 (1897), gives the melting point as 200°.

⁴ Werner and Bell, *J. Chem. Soc.*, **121**, 1790 (1922), describe a picrate, prepared from the reaction product of dicyandiamide and methylamine hydrochloride, which decomposes at 285° without melting.

The picrate is precipitated by the addition of a solution of sodium picrate to aqueous dimethylguanidine sulfate; after recrystallization from water, it melts sharply at $229-230^{\circ}.5$

Methyl Mercaptan Sodium Salt.—When methyl mercaptan is passed into a 25% solution of sodium hydroxide, absorption takes place with evolution of heat; after saturation, the solution on standing deposits flat needles which may attain a length of several centimeters. These crystals rapidly effloresce on exposure to air, apparently giving up water of crystallization. The salt is readily soluble in cold water and even more so in cold methyl alcohol. Although a boiling alkaline solution of methyl mercaptan (unlike ethyl mercaptan and its homologs) does not yield the free mercaptan in appreciable quantities to the distillate, the salt possesses a powerful odor; attempts to determine directly the percentage of water of crystallization were unsuccessful, owing to loss of substance other than moisture. When the crystals are heated above 200° decomposition sets in, sodium disulfide being formed in considerable amount.

Analyses. Subs., 0.5468: Na₂SO₄, 0.2540. Subs., 0.6584: NaCl, 0.2489. Calc. for 2CH₃SNa_.9H₂O: Na, 15.23. Calc. for CH₃SNa_.5H₂O: Na, 14.75. Found: Na, 15.04, 14.90.

Summary

A convenient method is described for the preparation of mono- and dialkylguanidines.

A description is given of 3 crystalline salts hitherto not mentioned in the literature: methylguanidine sulfate, α,α -dimethylguanidine sulfate, and the sodium salt of methyl mercaptan.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH, PARKE, DAVIS AND COMPANY, No. 16]

SOME DIALKYLBARBITURIC ACIDS WITH TERTIARY AMINO GROUPING

By Arthur W. Dox and Lester Yoder Received March 1, 1923

In continuation of the investigations in the barbituric acid series which have been in progress in this Laboratory during the past 2 years, it seemed worth while to prepare certain more complex derivatives for the purpose of studying their physiological activity. Previous work has shown that the dialkylbarbituric acids of the veronal type exhibit hypnotic properties over quite a range of molecular weight. Our aim was now to add to the dialkylbarbituric acid another grouping with known physiological activity, but united through a stable linkage so that the substance would not readily undergo hydrolysis and enable the two components to exert their separate activities independently. The phenomenon of "synergy," familiar to pharmacologists, has been studied rather extensively in the case of simple mixtures of physiologically active substances, but comparatively little

⁶ Schenck, Ref. 2, gives the melting point as 230°. Werner and Bell, Ref. 4, give 227°.

is known concerning the effect of combining two or more such substances in a stable union.

The derivatives described in this paper may be considered as dialkylbarbituric acids (5-ethyl-5-propyl- and 5-isoamyl-5-propyl-barbituric acids) with diethylamine, ethylaniline, acetanilide and phenacetin, respectively, attached to the γ -carbon of the propyl group.

The steps by which these syntheses were accomplished may be illustrated in the case of 5-ethyl-5-diethylamino-propyl-barbituric acid as follows,

$$\begin{array}{c} C_2H_5-CH(COOC_2H_5)_2 \longrightarrow Br(CH_2)_3 \\ C_2H_5-CH(COOC_2H_5)_2 \longrightarrow CCOOC_2H_5 \\ C_2H_5-COOC_2H_5 \longrightarrow CCOOC_2H_5 \end{array}$$

Experimental Part

In the double alkylation of ethyl malonate it is preferable to introduce the unsubstituted alkyl first. Otherwise, the alkylene bromide tends to form a cyclic derivative in which both reactive hydrogens of the ethyl malonate are substituted.1 Ethylene and trimethylene bromides are the only alkylene halides readily available. Attempts to introduce a β bromo-ethyl group by treatment of the alkyl malonic ester with ethylene bromide were much less successful than the introduction of the \gamma-bromopropyl group with trimethylene bromide. The latter was accordingly used throughout in these preparations. The yields, however, were smaller than those obtained in the preparation of the ordinary dialkylmalonic esters. The loss was obviously due to a side reaction in which hydrobromic acid is removed from the trimethylene bromide, giving allyl bromide which was easily recognized by its odor. By using benzene in place of alcohol, this difficulty was largely overcome, but a further loss was the formation of a considerable amount of a high-boiling product, probably a tetracarboxylic ester resulting from a reaction between 2 molecules of sodium alkylmalonic ester and 1 of trimethylene bromide. This secondary reaction was reduced to a minimum by the use of a great excess of trimethylene bromide. The alkyl-γ-bromopropyl-malonic esters then reacted readily with basic secondary amines and with the sodium salt of acvl amines to form alkyl-y-alkylaminopropyl-malonic esters, which in turn condensed with urea with ring closure giving the desired barbituric acids with alkylamine substitution on the γ-carbon of the propyl group.

Ethyl- γ -bromopropyl-malonate.—Twelve g. of finely divided sodium was gradually added to a cold solution of 95 g. of ethyl ethylmalonate in 250 cc. of anhydrous benzene. Practically all of the sodium dissolved with evolution of hydrogen. To the cold solution 200 g. (calc., 107 g.) of trimethylene bromide was added. The temperature of the cooling bath was gradually raised and finally the mixture was refluxed until it became neutral to litmus. The product was shaken with water to remove the sodium

¹ Dox and Yoder, This Journal, 43, 680, 1368, 2097 (1921).

bromide, then dried with calcium chloride and finally distilled under diminished pressure. The first portion of the distillate consisted of benzene, trimethylene bromide and ethyl ethylmalonate, then the condensation product came over between 160° and 180° at 20 mm., leaving about 8 g. of a high-boiling residue. After three fractionations, we obtained 50 g. of an oil boiling at 169–174° at 20 mm. pressure.

Analysis. Subs., 0. 1780: AgBr, 0.1037. Calc. for $C_{12}H_{21}O_4Br$: Br, 25.8. Found: 24.8.

Ethyl Ethyl- γ -diethylaminopropyl-malonate.—A mixture of 50 g. of ethyl ethyl- γ -bromopropyl-malonate and 30 g. of diethylamine was gently refluxed for 2 hours on a water-bath. Diethylammonium bromide separated rapidly at first. The reaction product was shaken with a concd. solution of sodium hydroxide and the latter drawn off through a funnel. The remaining oily layer was dried with solid sodium hydroxide and distilled under diminished pressure. After two fractionations, 40 g. of a yellow oil boiling at $143-149^{\circ}$ at 6 mm. pressure was collected.

Analyses. Subs., 0.2012, 0.2080: NH₃, 6.7, 6.9 cc. of 0.1 N acid. Calc. for $C_{16}H_{31}$ -O₄N: N, 4.65. Found: 4.66, 4.64.

5-Ethyl-5- γ -diethylaminopropyl-barbituric Acid.—A mixture of 10 g. of ethyl ethyl- γ -diethylaminopropyl-malonate, 3 g. of urea, and 40 cc. of absolute alcohol in which 2.5 g. of sodium had been dissolved, was heated in an autoclave at 108° for 7 hours. The white pasty product was made neutral to litmus by the addition of concd. hydrochloric acid, the precipitated sodium chloride removed by filtration, and the alcoholic filtrate evaporated to a sirup on the steam-bath. On the addition of sodium hydroxide solution, crystals of the barbituric acid separated, which were dried by suction and purified by recrystallization from water; yield, 3.5 g.; m. p., 165–166°. The substance is insoluble in strong alkali, ether or benzene but readily soluble in water or alcohol. It is basic and forms salts with acids.

Analyses. Subs., 0.2, 0.2: NH₃, 22.35, 22.35 cc. of 0.1 N acid. Calc. for $C_{13}H_{23}$ - O_3N_3 : N, 15.61. Found: 15.64, 15.64.

Ethyl- γ -acetanilinopropyl-malonate.—The sodium salt of acetanilide was first prepared by refluxing 9.5 g. of acetanilide in 200 cc. of anhydrous benzene with 1.6 g. of sodium. After this mixture cooled, 22 g. of ethyl ethyl- γ -bromopropyl-malonate was added and the suspension was gently heated under a reflux condenser for 12 hours. The sodium bromide was washed out with water, and the oil dried with calcium chloride and distilled. Fractionation gave 15 g. of a viscous yellow oil boiling at 244–250° at 17 mm.

Analyses. Subs., 0.2, 0.2: NH₃, 5.3, 5.4 cc. of 0.1 N acid. Calc. for $C_{20}H_{29}O_5N$: N, 3.85. Found: 3.71, 3.78.

5-Ethyl-5- γ -acetanilinopropyl-barbituric Acid.—To a solution of 2.5 g. of sodium in 40 cc. of absolute alcohol, 12 g. of ethyl ethyl- γ -acetanilinopropyl-malonate and 3 g. of urea were added. The mixture was heated in an autoclave at 108° for 7 hours. After neutralization with concd. hydrochloric acid the product was filtered and the filtrate evaporated to a small volume. Addition of water resulted in the separation of an oil which solidified after a time. This was recrystallized from benzene containing a little alcohol; yield, 9 g.; m. p., 180° The substance is readily soluble in alcohol, but sparingly soluble in benzene or hot water.

Analyses. Subs., 0.2, 0.2: NH₃, 18.0, 18.1 cc. of 0.1 N acid. Calc. for $C_{17}H_{21}O_4N_3$: N, 12.68. Found: 12.60, 12.67.

Ethyl Ethyl- γ -acetophenetidinopropyl-malonate.—Molecular proportions were used and the same procedure followed as that employed in the preparation of ethyl ethyl- γ -acetanilinopropyl-malonate, but with phenacetin in place of acetanilide. The

washed and dried oil was fractionated under diminished pressure, and the fraction boiling at 237–240° at 4 mm. was collected.

Analyses. Subs., 0.2, 0.2: NH₃, 4.7, 4.8 cc. of 0.1 N acid. Calc. for $C_{22}H_{33}O_6N$: N, 3.44. Found: 3.29, 3.36.

5-Ethyl-5- γ -acetophenetidinopropyl-barbituric Acid.—A solution of 13 g. of ethyl ethyl- γ -acetophenetidinopropyl-malonate and 3 g. of urea in 40 cc. of absolute alcohol containing 2.5 g. of sodium was heated in an autoclave at 108° for 7 hours. The alcoholic filtrate from the neutralized and filtered mixture was evaporated to a small volume and then diluted with water until no more oil separated. Some unchanged ester which interfered with crystallization was removed by treatment with alkali and extraction with ether. The alkaline solution was then neutralized and warmed for a short time on the steam-bath until the product began to crystallize. After recrystallization from benzene containing a small amount of alcohol, 8.8 g. of a product melting at 158–159° was obtained. The substance is very soluble in alcohol, but only sparingly soluble in benzene or hot water.

Analyses. Subs., 0.2, 0.2: NH₃, 15.9, 16.0 cc. of 0.1 N acid. Calc. for $C_{19}H_{25}O_5N_3$: N, 11.20. Found: 11.13, 11.20.

Ethyl isoAmyl- γ -bromopropyl-malonate.—A solution of 75 g. of ethyl isoamyl-malonate in 150 cc. of benzene was cooled and 7.7 g. of finely divided sodium was added. After the sodium had dissolved, 135 g. of trimethylene bromide was added and the mixture was heated in a bath at about 85° for 2 hours, until the reaction of the solution was neutral, when the mixture was washed, dried and distilled in a vacuum. Two fractionations gave 50 g. of a viscous oil boiling at 175–182° at 13 mm. About 25 g. of a higher-boiling residue remained in the distilling flask.

Analysis. Subs., 0.1589: AgBr, 0.0815. Calc. for $C_{15}H_{27}O_4Br$: Br, 22.7. Found: 21.8.

Ethyl isoAmyl- γ -diethylaminopropyl-malonate.—A solution of 36 g. of ethyl isoamyl- γ -bromopropyl-malonate in 20 g. of diethylamine was refluxed for 4 hours. A copious separation of diethylammonium bromide occurred. The mixture was washed and dried, as in the preparation of the corresponding ethyl derivative, and fractionated twice, yielding 29 g. of a thick yellow oil that boiled at $155-161^\circ$ at 5 mm.

Analyses. Subs., 0.25, 0.25: NH₃, 6.7, 6.9 cc. of 0.1 N acid. Calc. for $C_{19}H_{a7}O_4N$: N, 4.08. Found: 3.76, 3.87.

5-isoAmyl-5- γ -diethylaminopropyl-barbituric Acid.—A solution of 11 g. of ethyl isoamyl- γ -diethylaminopropyl-malonate and 3 g. of urea in 40 cc. of absolute alcohol containing 2.5 g. of sodium was heated in an autoclave at 108° for 7 hours. To the white pasty mass thus obtained, coned. hydrochloric acid was added until the reaction was neutral, the sodium chloride was removed by filtration and the alcoholic filtrate evaporated to a sirup. Upon the addition of water an oil separated which consisted largely of unchanged ester and was discarded. The aqueous solution was evaporated to crystallization and finally yielded 5 g. of a product melting at 133°. This isoamyl derivative is somewhat less soluble in water and more soluble in alcohol, ether or benzene than the homologous ethyl derivative described above.

Analyses. Subs., 0.2, 0.2: NH₃, 18.95, 18.90 cc. of 0.1 N acid. Calc. for $C_{16}H_{29}$ - O_3N_3 : N, 13.50. Found: 13.30, 13.26.

Ethyl isoAmyl- γ -ethylanilinopropyl-malonate.—A mixture of 25 g. of ethyl isoamyl- γ -bromopropyl-malonate and 18 g. of ethylaniline was heated in an oil-bath at 160° for 4 hours. The dark, viscous oil was washed with dil. sodium hydroxide solution, then with water, dried with solid sodium hydroxide and distilled; 15 g. of a yellow oil boiling at 194-201° at 4 mm. was collected.

Analyses. Subs., 0.2, 0.2: NH₃, 5.0, 5.0 cc. of 0.1 N acid. Calc. for $C_{23}H_{57}O_4N$: N, 3.58. Found: 3.50, 3.50.

5-isoAmyl-5- γ -ethylanilinopropyl-barbituric Acid.—A solution of 10 g. of ethyl isoamyl- γ -ethylanilinopropyl-malonate and 2.5 g. of urea in 40 cc. of absolute alcohol containing 2 g. of sodium was heated in an autoclave at 108° for 7 hours. The product was neutralized with hydrochloric acid, the chlorides were removed by filtration and the alcoholic filtrate concentrated to a sirup. On the addition of water, an oil separated. This failed to crystallize until the impurities had been removed by extraction of the alkaline solution with ether. The oil obtained by acidifying the alkaline solution was dissolved in benzene, and the addition of ligroin then caused the product to separate gradually in needle-shaped crystals; yield, 3 g.; m. p., 135°. The substance is insoluble in water, but readily soluble in benzene, ether or alcohol.

Analyses. Subs., 0.2, 0.2: NH₃, 16.0, 16.2 cc. of 0.1 N acid. Calc. for $C_{20}H_{29}O_2N_8$: N, 11.69. Found: 11.20, 11.34.

Ethyl isoAmyl- γ -acetophenetidinopropyl-malonate.—The sodium salt of phenacetin was first prepared by refluxing a solution of 12.5 g. of phenacetin in 200 cc. of benzene with 1.6 g. of finely divided sodium. To the suspended sodium salt 24 g. of ethyl isoamyl- γ -bromopropyl-malonate was added, and the mixture was refluxed for several hours until it was neutral to litmus. The sodium bromide was removed with water and the oily layer dried with calcium chloride. Two fractionations under diminished pressure gave 18 g. of a viscous, yellow oil boiling at 245–250° at 4 mm.

Analyses. Subs., 0.2, 0.2: NH₃, 4.4, 4.3 cc. of 0.1 N acid. Calc. for $C_{25}H_{39}O_6N$: N, 3.12. Found: 3.08, 3.01.

5-isoAmyl-5- γ -acetophenetidinopropyl-barbituric Acid.—A solution of 10 g. of ethyl isoamyl- γ -acetophenetidinopropyl-malonate and 2.5 g. of urea in 40 cc. of absolute alcohol containing 2 g. of sodium was heated in an autoclave at 108° for 7 hours. The product was neutralized and filtered as usual and evaporated to a sirup. The addition of water resulted in the separation of the barbituric acid in small crystals. These were dried and recrystallized from benzene containing a little alcohol; yield, 5 g.; m. p., 155°. The substance is practically insoluble in hot water, slightly soluble in benzene, and readily soluble in alcohol. The acetyl group is not easily split off. After successive treatment with hot alkali and concd. hydrochloric acid the original substance was recovered.

Analyses. Subs., 0.1, 0.1: NH₃, 7.2, 7.3 cc. of 0.1 N acid. Calc. for $C_{22}H_{31}O_5N_3$: N, 10.07. Found: 10.08, 10.22.

Physiological Properties

The barbituric acids described above have a bitter taste similar to that of veronal. Some were tested physiologically by oral administration to dogs, others by intraperitoneal injection of the alkali solution into white mice. Only the possibility of sedative action was considered in these preliminary tests. The following results recorded by way of illustration are typical.

Barbituric acid	Dose G.	Wt. of dog Kg.	Effect
Ethyl-γ-acetophenetidinopropyl	2	16	slight drowsiness
Ethyl-γ-diethylaminopropyl	2	15	none
isoAmyl-γ-acetophenetidinopropyl	1.8	15	none

It will be noted from the foregoing descriptions that the basic diethylamino derivatives are soluble in water but insoluble in neutral organic

solvents other than alcohol. The distribution coefficient is, therefore, less than unity. On the other hand, the neutral derivatives are practically insoluble in water. In the case of the phenacetin derivatives a possible antagonistic action of the two components was shown to be negligible. A mixture of 1 g. of dipropylbarbituric acid with 0.8 g. of phenacetin produced a very pronounced hypnotic effect on a dog of 18 kg. The explanation of the lack of hypnotic properties of these complex barbituric acids is, we believe, in some cases their insolubility which prevents absorption and their stability which precludes the possibility of hydrolysis at the point of union of the two components, and in others, the reversal of the distribution coefficient. Similarly, the intraperitoneal injection of the sodium salts into mice in doses twice as large as the effective dose of veronal produced no noteworthy symptoms, except in the case of 5-isoamyl-5-γ-diethylaminopropyl-barbituric acid which appeared to be toxic without preliminary sedative action. Even when the substance is administered as the sodium salt, we have reason to believe that the actual absorption takes place in the form of the free acid, and is too slow to produce any noteworthy effect. This explanation is in harmony with the Overton-Mever theory of narcosis, according to which a substance must have a certain distribution coefficient between the two solvents water and fat (or lipoids) in order to exert hypnotic action. This of course applies strictly only to the synthetic hypnotics, none of which appear to exert any specific action upon the higher brain centers. By increasing the complexity of the dialkylbarbituric acids the solubility in water is reduced to a minimum beyond which absorption is too slow to result in the phenomenon of hypnosis, or if a strongly basic grouping has been introduced, the distribution coefficient becomes less than unity.

Summary

A number of ethyl dialkylmalonates have been prepared in which one alkyl is ethyl or isoamyl and the other n-propyl with substitution of a tertiary amino group on the γ -carbon. From these esters the corresponding barbituric acids have been prepared. The latter, when tested physiologically, failed to show the hypnotic effect characteristic of the simple dialkylbarbituric acids. This inactivity is attributed in some instances to insolubility and consequent failure of absorption, in others, to a reversal of the distribution coefficient.

DETROIT, MICHIGAN

[Contribution from the Bureau of Chemistry, United States Department of Agriculture]

METHYL AND ETHYL AMMONIUM-MERCURIC BROMIDES

By Raymond M. Hann

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Woodward and Alsberg¹ have pointed out the fact that tertiary alkyl amines in $0.1\,N$ concentration are readily precipitated as tri-alkyl ammonium-mercuric iodides by the addition of Mayer's reagent (potassium mercuric iodide) and have used this fact as a basis for the separation of tertiary from the primary and secondary amines. As a sequel to this research, Jamieson and Wherry² have prepared and described a series of methyl and ethyl ammonium-mercuric iodides, and have further extended the method to the crystallographic identification of the addition products, a procedure now commonly used in this Bureau as a confirmatory analytical step in the separation of amines. Barker and Porter³ have also contributed to the subject by a description of a number of the higher homologous quaternary ammonium-mercuric iodides.

The present work was undertaken at the suggestion of Dr. Edgar T. Wherry, Crystallographer of the Bureau of Chemistry, in order to complete the series of alkyl ammonium-mercuric halides and to determine the feasibility of using the alkyl substituted bromides in place of the corresponding iodides for the separation and identification of alkyl amines.

Unfortunately, the extreme solubility of all the alkyl ammoniummercuric bromides in common solvents precludes their use in determining amines. While the iodides usually are formed by addition of 1 molecule of alkyl ammonium bromide to 1 of metal bromide, the bromides tend to combine in the ratio of 1 to 2.

Numerous experimental difficulties were encountered in making the substances described. Preliminary attempts to make them in alcohol-acetone solution from alkyl halide, metal bromide and amine hydrochloride resulted in indefinite mixtures of alkyl ammonium-mercuric chlorides and bromides.

The compounds were finally obtained by the use of the hydrobromide of the amine in alcoholic solution according to the following equation: $R_2NH.HBr + RBr + HgBr_2 \longrightarrow R_3NHBr.HgBr_2 + HBr$. Concentration of the alcoholic solution gave crystals which, in a few cases, were suitable for crystallographic measurement.⁴

Experimental Part

1,2-Dimethylammonium-mercuric Bromide, (CH₃)₂NH₂Br.2HgBr₂.—Thirty-five g. of mercuric bromide suspended in 300 cc. of absolute ethyl alcohol was treated with ab-

¹ Woodward and Alsberg, J. Biol. Chem., 46, 1 (1921).

² Jamieson and Wherry, This Journal, 42, 136 (1920).

³ Barker and Porter, J. Chem. Soc., 117, 1303 (1920).

⁴ Reserved for publication by Dr. E. T. Wherry.

divided silver we found that it was possible to remove the chlorine from each of the 3 carbinol chlorides by allowing the substances to react for 20 minutes; only a trace of nuclear bromine was removed during this time. We did not succeed in isolating the resulting free radicals in a crystalline state, but their actual existence in their respective solutions was proved by the fact that oxygen was absorbed quantitatively in accordance with the equation, $(BrC_6H_4)R_2C-+O_2=(BrC_6H_4)R_2C-O-O-CR_2(C_6H_4Br)$; the resulting peroxides were isolated and analyzed. Iodine was absorbed by the solutions of the radicals, and the iodides of the general type, R_3CI , were produced.

It is now obvious that the removal of the nuclear bromine by the silver must occur subsequently to the removal of the carbinol chlorine; that is, the bromine is removed, not from the bromotriarylcarbinol chlorides themselves, but from the free radicals which have resulted from the initial action of the silver on the carbinol chlorides.

Such a mobility of bromine in the phenyl nucleus is especially remarkable in view of the fact that not even a trace of bromine is removed by silver from such compounds as $R_2(BrC_6H_4)C-X$, where X represents H, OH, OC_2H_5 or other similar groups. It is only when the valence, which is otherwise attached to X, becomes free that the bromine in the phenyl nucleus becomes labile toward metallic silver.

No rational explanation can be advanced for such a marked change in the stability of the nuclear bromine if the structure I is accepted for the radical p-bromotriphenylmethyl. However, if the existence of a dynamic equilibrium between a benzenoid and some quinonoid structure such as II, is assumed we then have a plausible explanation for the lability of the bromine. It is evident that the carbon atom C*, in II, must have different

$$R_2C = \underbrace{\hspace{1cm}}^{*} \underbrace{\hspace{1cm}}^{*} R_2 \underbrace{\hspace{1cm}}^{*} \underbrace{\hspace{1cm}}^{*} Br \underbrace{\hspace{1cm}}^{*} \underbrace{\hspace{1cm}}^{*} Br \underbrace{\hspace{1cm}}^{*} Br \underbrace{\hspace{1cm}}^{*} Br$$

properties from those which it possessed when it was part of a benzenoid nucleus; it should now function, to some extent, as though it were an aliphatic rather than an aromatic carbon atom and the bromine which is attached to it should, therefore, be removable by silver.

The problem, however, assumes greater complexity when the mobility of nuclear halogen in the brominated free radicals is studied quantitatively. It had been previously found⁴ that even under the most favorable conditions only $^{1}/_{2}$ of the total amount of nuclear bromine is removed from p-bromotriphenylcarbinol chloride. We have now established a similar behavior for the other two p-brominated carbinol chlorides previously mentioned; presumably this phenomenon is characteristic for all triarylmethyls that contain a bromine atom in the para position to the methane

carbon atom. It seems to us that without the aid of the quinonoid hypothesis it would be impossible to explain why only a fraction, and moreover, a very definite fraction of the total bromine is removed from the bromotriarylmethyls.

When a radical of the type under discussion is produced, the following factors must be taken into consideration: in addition to the dynamic equilibrium, existing between the unimolecular forms I, II and III, there is undoubtedly a state of equilibrium operating between these unimolecular and various bimolecular forms; there is no valid reason for assuming that the ordinary hexa-arylethane is the only bimolecular form possible. On the contrary, it is only rational to assume that union, with the formation of a bimolecular radical, may take place between I and I, or between any two of the unimolecular tautomers, 6 forms of R_6C_2 being possible.

Now it is evident that a bimolecular form, resulting from the union of I and I, III and III or I and III would not contain mobile bromine atoms; in a combination of II and II both bromine atoms would be equally labile and, therefore, both would be removable by silver. It is only when combination has taken place between I and II or II and III that one of the two bromine atoms in the resulting compound is linked to a quinonoid nucleus and is, therefore, labile while the second bromine remains attached to a true benzenoid ring. Consequently, if either one of these latter two bimolecular forms is present, in the complex system of tautomers which may result when a p-bromotriarylmethyl is formed, it then becomes possible to account for the very remarkable fact that $^{1}/_{2}$, and no more than $^{1}/_{2}$, of the total bromine is removed by the molecular silver.

If it is assumed, for example, that the principal component in solution, with respect to reactivity toward molecular silver, is IV (that is, I + II) the result of the interaction with silver would be as follows:

$$\begin{bmatrix} R_2C & & B_r & R_2C & & B_r & B_$$

Removal of the labile bromine, by metal, from IV leads to the formation of V which contains a trivalent carbon atom in the nucleus, thus making this compound analogous to II; since II is in tautomeric equilibrium with I, in a similar way V must be in equilibrium with VI. The latter substance (VI) may be designated as a free radical of "the second order," $R_8C-C_6H_4-CR_2$, while I represents a free radical of "the first order," R_3C .

When a mole of p-bromotriphenylcarbinol chloride, in solution, is converted into the radical of the first order, the solution, in accordance with the equation previously given, should absorb an amount of oxygen in agreement with the following ratio; 1 mole of oxygen for each 2 moles of the brominated triarylcarbinol chloride. When, however, prolonged reaction with the metal has resulted in the formation of the radical of the second order (VI), then only $^{1}/_{2}$ of that amount of oxygen which has been required by Radical I is necessary for the formation of the peroxide (VII) which corresponds to Radical VI.

Experiments have conclusively established the validity of this assumption. It was found that when chlorine alone was removed from the triarylcarbinol chloride the subsequent absorption of oxygen was, as anticipated, 1 mole of oxygen for 2 moles of R₃C-Cl; but when, in addition

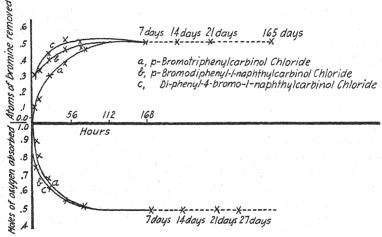


Fig. 1.—The relation between increase of nuclear bromine removed and the corresponding decrease of the amount of oxygen absorbed by the radicals

to the chlorine, the full $^1/_2$ of the nuclear bromine was eliminated the subsequent absorption of oxygen was found to be only $^1/_2$ mole for 2 moles of R₃C–Cl. Finally, when only a part of the total possible $^1/_2$ gram atom of bromine was removed, the amount of oxygen absorbed was also a corresponding fraction between 1 mole and $^1/_2$ mole.

The curves of Fig. 1, which have been constructed from data in Tables I, II and III given in the experimental part of this paper, show the concordance between these two phenomena; increase in the quantity of nuclear bromine removed is paralleled by a decrease in the amount of oxygen which the reaction product was capable of absorbing.

In further confirmation of the above hypothesis concerning the mechanism of the reaction, we have isolated the peroxides, corresponding to the radicals of the second order, in the case of each of the 3 p-bromotriarylmethylcarbinol chlorides. All our attempts to isolate the free radicals themselves in crystalline condition proved unsuccessful; these radicals appear to be extremely sensitive to various influences, and upon concentration of their respective solutions they were either polymerized or decomposed into inert substances.

Another phenomenon, namely, a change in color, indicates a change of the free radical of the first order into the radical of the second order. With the elimination of chlorine from *p*-bromodiphenyl-1-naphthylcarbinol chloride there was formed a blue-violet solution, resembling an aqueous solution of potassium permanganate; upon the removal of nuclear bromine the color gradually changed into an intense blue.

It seems to us that the results we have obtained leave no alternative to the conclusion that the p-bromotriarylmethyls exist, not only in a benzenoid state but also in a quinonoid modification; union of the two types gives rise to a bimolecular combination, the constitution of which is tautomeric with the ordinary, bimolecular hexa-arylethane.

If the phenomenon of quinoidation is accepted for the *p*-bromotriarylmethyls, must it not be equally operative in the case of other, halogen-free radicals of the triarylmethyl type?

Salt-like Derivatives.—In discussing the salt-like derivatives of the triarylcarbinols it must be remembered that only combinations between the carbinols and certain acids produce colored compounds; with hydrochloric and hydrobromic acids, colorless chlorides and bromides are produced; combinations with the organic acids, studied so far, are devoid of color. On the other hand, the carbinol sulfates, sulfites, nitrates, perchlorates and phosphates all possess color, some of these derivatives being as intensely colored as the triphenylmethane dyes themselves.

It has been shown that the nuclear halogen is not removed from the colorless, salt-like derivatives, even to the slightest extent, by contact with silver salts. However, in the case of the *colored*, *para*-halogenated triarylcarbinol derivatives, such as the sulfates, the halogen in the aromatic nucleus is readily removed by silver sulfate. Here, again, the mobility of the nuclear halogen finds its best explanation in the assumption of a quinonoid chromophore in the molecule.

Silver sulfate removes 1 atom of chlorine and, subsequently, 1 whole atom of bromine from 1 molecule of p-bromotriphenylcarbinol chloride.⁶ The mechanism of this reaction can be formulated as follows: first, the carbinol chlorine is removed, resulting in the formation of the colorless carbinol sulfate (VIII); this tautomerizes instantly into the colored sulfate (IX). The bromine, being now attached to a carbon atom (C*),

⁵ Hantzsch, Ber., 54, 2577 (1921).

⁶ Gomberg, ibid., 40, 1852 (1907).

essentially aliphatic in nature, becomes reactive toward silver sulfate, and there results a colored, para-quinonoid sulfate (X).

This interpretation of the experimental results according to the quinon-oid hypothesis was, at one time, challenged by v. Baeyer⁷ who stated that the formation of silver bromide did not necessarily indicate that the compound X had been formed; according to him the silver halide might have been produced during a disruption of the triarylmethyl nucleus. We have now been able to prove, in a very decisive manner, that v. Baeyer's criticism is not valid. We have shown that in the case of each of the 3 bromocarbinol sulfates the bromine is actually removed by the silver sulfate, approximately 1 whole atom of bromine from each R₃C-X. Moreover, the reaction mixture, on hydrolysis, yields the corresponding p-hydroxytriarylcarbinol XI and XII, and this has been identified in both the benzenoid and the quinonoid state. It is, therefore, evident that, both subsequent as well as prior to the removal of the para bromine, the triarylmethyl nucleus remains intact.

Thus, just as in the case of the colored triarylmethyls, the mobility of nuclear halogen in the colored salts also is logically explained by the assumption of a quinonoid constitution. The inference is fully justified that the colored triarylcarbinol sulfates, in general, regardless of whether or not they contain nuclear halogen, must be quinonoid.

Experimental Part

Preparation of Materials

para-Bromotriphenylcarbinol Chloride

The Carbinol, $(Br_{\theta}CH_{4})(C_{\theta}H_{5})_{2}C$ —OH.—This carbinol was prepared by the action of phenylmagnesium bromide on p-bromobenzophenone^{3a} and also by the interaction of phenylmagnesium bromide and the methyl ester of p-bromobenzoic acid.^{3b}

Since the resulting crude carbinol was an oil and consequently difficult to purify, it was converted by means of hydrogen chloride into the corresponding crystalline chloride. From the pure chloride the carbinol was readily obtained by the following process. Three g. of the chloride, 8 cc. of acetone, 1.2 cc. of dimethyl aniline and 2 cc. of water were refluxed for $^{1}/_{2}$ hour. The acetone was removed on a steam-bath and the viscous residue was freed from dimethylaniline hydrochloride by washing with water. When the product was stirred with a small amount of carbon disulfide the material quickly be-

⁷ Baeyer, Ber., 40, 3085 (1907).

came crystalline. After recrystallization from glacial acetic acid the carbinol was found to melt at $102-103^{\circ}$; this temperature is 30° higher than that recorded in the literature. Recrystallization from other solvents such as petroleum ether did not change the melting point. The compound dissolves very readily in benzene, in ether, in acetone and in carbon disulfide; with coned. sulfuric acid an orange-red solution is formed.

The Chloride.—The pure carbinol was dissolved in the smallest possible amount of absolute ether and the solution was then saturated with hydrogen chloride. The carbinol chloride soon precipitated; after several hours, the chloride was collected and then thoroughly dried over soda lime and sulfuric acid in a vacuum desiccator. The chloride melted at 112-114°, as recorded in the literature.

para-Bromodiphenyl-1-naphthylcarbinol Chloride

The Carbinol, $(BrC_6H_4)(C_6H_5)(C_{10}H_7)C$ —OH.—A solution of 1-naphthylmagnesium bromide was prepared from 4.0 g. of magnesium turnings, which had been etched with a small amount of iodine, 125 cc. of absolute ether and 25 cc. of 1-naphthyl bromide. Forty g. of p-bromobenzophenone, dissolved in 50 cc. of warm benzene, was added to this solution and the mixture was then heated for 5 hours in a bath. When the magnesium addition product settled out it was collected on a filter, thoroughly washed with benzene and then decomposed with ice and a small amount of acid in the usual manner. The carbinol was then obtained at once quite pure. When the magnesium addition product failed to precipitate, the reaction mixture, after treatment with ice and acid, was distilled with steam in order to remove the solvent and any unchanged ketone. The crude carbinol was then recrystallized from carbon disulfide. The yield, based on the ketone, was 80%. The carbinol melts at $132-133^\circ$. It dissolves readily in ether, benzene and warm alcohol and is colored an intense green by concd. sulfuric or perchloric acid.

Analysis. Calc. for C23H17OBr: Br, 20.55. Found: 20.72.

The Chloride.—A warm, concentrated solution of the carbinol in benzene was saturated with hydrogen chloride. After 36 hours most of the chloride had precipitated. The hydrochloric acid, produced from the water formed during the reaction and the excess of hydrogen chloride, was removed by means of a pipet and the carbinol chloride was quickly filtered on a Büchner funnel. The material was washed several times with absolute ether and finally suspended in ether to remove the last traces of acid. After 24 hours the chloride was filtered and dried in a vacuum desiccator over sulfuric acid and soda lime; m. p., 182–183°.

The carbinol chloride combines with the chlorides of such metals as zinc, tin, iron, mercury and aluminum, forming intensely colored, green addition products.

Analyses. Calc. for $C_{23}H_{16}ClBr$: C, 67.75; H, 3.93; Cl, 8.70; Br, 19.62. Found: C, 67.53; H, 4.02; Cl, 8.84; Br, 19.83.

p-Bromophenyl-chrysofluorene.—The carbinol, as well as the corresponding chloride, when heated with glacial acetic and coned. sulfuric acids, loses 1 molecule of water or 1 molecule of hydrogen chloride and is converted into a fluorene.

That the latter has Constitution XIII, rather than XIV or XV, was proved by carrying out the reactions indicated below.

Fifty cc. of boiling glacial acetic acid was mixed with 10 g. of the carbinol and the mixture was heated until the carbinol had completely dissolved. Two cc. of concd. sulfuric acid was then added and the solution was vigorously stirred; the latter became deep green and the fluorene precipitated almost instantly. After the mixture had cooled, water was added and the material was filtered and washed; yield, 6.1 g. The compound, recrystallized from xylene, melts at 233–235°. The fluorene is only slightly soluble in the ordinary organic solvents and is not colored by concd. sulfuric acid.

Analysis. Calc. for C23H15Br: Br, 21.54. Found: 21.60.

A mixture of 1.9 g. of fluorene, 50 cc. of glacial acetic acid and 12 g. of sodium dichromate was refluxed for $2^1/_2$ hours, and then poured into 200 cc. of hot water, whereupon 0.9 g. of a yellow substance, the quinone XVII, was precipitated. The material was filtered and from the filtrate there was deposited, after 36 hours, 0.2 g. of the colorless, crystalline 4'-bromobenzoyl-2-benzoic acid (XVIII) which melted at $167-168^{\circ}$. The melting point given in the literature⁸ is 169° .

The crystalline quinone, after several recrystallizations from glacial acetic acid, melted at 172–173°. It was found to be quite soluble in benzene, acetone or carbon disulfide; it dissolved in coned. sulfuric acid with the formation of a blood-red solution.

Analyses. Calc. for $C_{23}H_{13}O_{2}Br$: C, 66.19; H, 3.14; Br, 19.17. Found: C, 66.22; H, 3.21; Br, 19.02.

In conformity with its constitution as a quinone, the compound liberates iodine when treated with a mixture of potassium iodide, alcohol and hydrochloric acid.9

That the quinone is an intermediate product in the oxidation of the fluorene to the benzoyl-benzoic acid is proved by the fact that oxidation converts it almost quantitatively into the above-mentioned acid. To a boiling solution of 0.3 g. of the yellow material in 30 cc. of glacial acetic acid 1 g. of chromic anhydride was added during the course of an hour. The reaction mixture was then poured into 50 cc. of water and the mixture filtered. The filtrate was partly neutralized with sodium hydroxide and then extracted a number of times with ether. The ether extracts yielded 0.17 g. of the crystalline bromobenzoyl-benzoic acid.

Diphenyl-4-bromo-1-naphthylcarbinol Chloride

4-Bromo-1-cyanonaphthalene.—This substance, required for the preparation of the carbinol, was prepared as follows: 1-aminonaphthalene was acetylated¹⁰ and the resulting 1-acetylaminonaphthalene was brominated.¹¹ The 4-bromo-1-acetylaminonaphthalene thus prepared was boiled with alcohol and hydrochloric acid and thereby hy-

⁸ Ger. pat., 148,110.

⁹ Valeur, Compt. rend., 129, 522 (1899).

¹⁰ Weyl, "Methoden der Organischen Chemie," Verlag G. Thieme, Leipzig, 1911, II, 1273.

¹¹ Rother, Ber., 4, 850 (1871).

drolyzed into 4-bromo-1-aminonaphthalene. Upon recrystallization from gasoline this substance was obtained in the form of colorless crystals which melt at 102°,12

Twenty-two g. of the bromo-amine was added to glacial acetic acid which contained hydrogen chloride somewhat in excess of that required theoretically to convert the amine into the hydrochloride; the amine hydrochloride settled, with the liberation of heat, in the form of a paste. The latter was thoroughly stirred and the warm mixture then cooled to 15°. Eighteen cc. of amyl nitrite was added, all in one portion, the mixture being vigorously stirred and the temperature kept below 25°. After a short time all of the material had dissolved and only a very small amount of nitrogen was evolved. The clear acetic acid solution of the diazonium chloride was poured, a little at a time, with constant stirring, into 300 cc. of absolute ether which had previously been cooled to 0°. The diazonium chloride separated as an oil which quickly solidified to a light yellow, crystalline product. The liquid was decanted, the precipitate washed with cold ether and then filtered and quickly air-dried. The diazonium salt, which weighed about 20 g., was dissolved at once in 400 cc. of ice water.

The conversion of the dissolved material into the cyanide was effected by adding it slowly, well below the surface, to a clear solution of cuprous cyanide, prepared from 75 g. of copper sulfate in 300 cc. of water and 81 g. of potassium cyanide in 180 cc. of water. During this addition, carried out in a 3-neck, 2-liter round-bottom flask, the mixture was vigorously stirred mechanically and the temperature held at 80°. After all of the diazonium solution had been added the stirring was continued for 1/2 hour. When the mixture had cooled the liquid was decanted from the brown, crystalline material and the latter was then washed with water and dried. The cyanide was extracted from the crude reaction product with glacial acetic acid, the extracts were concentrated and the cyanide was precipitated by the addition of water. The yield was 18 g., or 80%. It was found unnecessary to purify the cyanide further in order to convert it into the corresponding carboxylic acid. The pure cyanide is soluble in benzene and in warm alcohol, and melts at $102-103^\circ$.

4-Bromo-1-naphthalenecarboxylic Acid.—The crude cyanide was refluxed for 12 hours with a mixture consisting of equal parts of water, glacial acetic acid and coned. sulfuric acid. The reaction mixture was then poured into water and the acid was separated from unchanged cyanide by extraction of the precipitated material with dil. sodium carbonate solution. The clear, alkaline solution was then acidified with hydrochloric acid and the bromonaphthoic acid obtained in the form of colorless crystals. The acid is soluble in alcohol and acetic acid; m. p., 13 217–220°.

Analyses. Calc. for C₁₁H₇O₂Br: C, 52.61; H, 2.81; Br, 31.85. Found: C, 52.46; H, 2.80; Br, 31.19.

Ethyl Ester of 4-Bromo-1-naphthalenecarboxylic Acid.—Fifty g. of the acid was dissolved in 600 cc. of absolute alcohol and the solution then partly saturated with hydrogen chloride; the mixture was refluxed for 16 hours. After removal of about $^2/_3$ of the alcohol under reduced pressure the residue was poured into 3.5 liters of ice water; the resulting oil soon solidified. The ester was washed with dilute aqueous sodium carbonate and then air-dried. Since it is extremely soluble in the usual organic solvents the ester could not be recrystallized; it was purified by dissolving it in low-boiling petroleum ether, filtering and then allowing the solvent to evaporate spontaneously. The yield was 56 g., or 90%; m. p., $42-43^\circ$.

¹² Morawski and Gläser, *Monatsh.*, 9, 293 (1888).

¹³ This compound has been recorded in the literature, since the completion of this work, by Mayer and Sieglitz, *Ber.*, 55, 1841 (1922). The method used by these investigators is not, however, a preparative one. The melting point is given as 212°.

Diphenyl-4-bromo-1-naphthyl Carbinol, $(C_6H_5)_2(BrC_{10}H_6)C$ —OH.—A solution of phenylmagnesium bromide was prepared from 10.2 g. of magnesium turnings, 45 cc. of bromobenzene and 100 cc. of ether. The ether was removed under diminished pressure and 35 cc. of dry toluene was then poured on the sirupy phenylmagnesium bromide; 15 g. of the ethyl 4-bromo-1-naphthalate dissolved in 50 cc. of dry toluene was added and the mixture gently refluxed for 4 hours. The reaction mixture was decomposed, the toluene layer separated and the toluene removed by steam distillation. The solid, slightly yellow carbinol thus obtained was dissolved in alcohol-free ether and converted directly into the carbinol chloride as described below. The yield of crude carbinol, based on the ester, was 60%.

The pure carbinol was obtained from the carbinol chloride by refluxing, for 45 minutes, a mixture of 8.2 g. of the pure chloride, 2.6 g. of dimethyl aniline, 50 cc. of acetone and 8 cc. of water. The reaction mixture was then freed from acetone and dimethylaniline hydrochloride. The carbinol was recrystallized from ether with the addition of a small amount of petroleum ether. It was obtained in the form of colorless crystals; m. p., 130°.

Analyses. Calc. for C₂₃H₁₇OBr: C, 70.95; H, 4.40; Br, 20.55. Found: C, 71.14; H, 4.37; Br, 19.71.

The Chloride.—A concentrated solution of the carbinol in absolute ether was saturated with hydrogen chloride, whereupon the carbinol chloride began to precipitate. After 24 hours the liquid was decanted from the crystals, the latter transferred to a Büchner funnel, washed with a small amount of absolute ether and then dried in a vacuum desiccator over sulfuric acid and soda lime. The chloride was further purified by recrystallization from benzene with the addition of an equal volume of low-boiling petroleum ether; m. p., 160–161°; it dissolves in concd. sulfuric acid, forming a deep green solution.

Analysis. Hydrolyzable Cl, Calc.: 8.7%. Found: 8.4%.

Reaction between Molecular Silver and the Carbinol Chlorides

The Radicals from p-Bromotriphenylcarbinol Chloride.—A number of tubes, each containing $1.000~\rm g$. of pure carbinol chloride, $3.0~\rm g$. of 20-mesh, molecular silver and $30~\rm cc$. of xylene, were rotated at room temperature for various periods of time.

A second series of tubes was prepared, identical with those described above with the exception that bromobenzene was used as a solvent instead of xylene, the latter having been used because of its comparatively low vapor pressure. After rotation for a definite period of time a tube from the first series was opened and the amount of silver halides was determined; a tube from the second series, rotated for an equal period of time, was placed in an apparatus designed for the measurement of absorbed oxygen.¹⁴

As the following table shows, the radical of the first order was formed quantitatively, after rotation for 20 minutes, and the solution of the radical absorbed approximately the calculated amount of oxygen. Upon further reaction of the silver the nuclear bromine was slowly removed with the gradual formation of the radical of the second order; the amount of oxygen, which the tubes were then capable of absorbing, gradually

¹⁴ Gomberg and Schoepfle, This Journal, 39, 1661 (1917).

decreased until a fairly constant value—1/2 of the amount found for the first radical—was obtained.

TABLE I

REMOVAL OF CARBINOL CHLORINE AND NUCLEAR BROMINE BY SILVER AND ESTIMATION OF CAPACITY OF THE RESULTING RADICALS FOR ABSORBING OXYGEN

Calculated absorption for Radical of the First Order, 31.2 cc.; for Radical of the Second Order, 15.6 cc.

Time rotated Hours	Halogen Ato		Observed absorption of oxygen. Cc., N. T. P.	Time rotated Hours	Halogen At Cl	removed oms Br	Observed absorption of oxygen. Cc., N. T. P.
$^{1}/_{3}$	0.97	0.01	33.2	48	1.01	0.36	17.2
1	0.96	0.01	31.8	72	1.00	0.46	15.0
4	0.98	0.08	27.8	1 week	0.98	0.48	16.0
12	0.96	0.12	24.6	2 weeks	1.05	0.48	15.4
24	0.98	0.27	20.6	3 weeks	1.01	0.51	14.8

p-Bromotriphenylmethyl Peroxide, $[(C_6H_4Br)(C_6H_5)_2C]_2O_2$.—After the reaction mixture had rotated for 20 minutes, in absolute ether as a solvent and with exposure to the air, the peroxide was formed. It melted at 167° and was identical with the peroxide which is formed by the simultaneous action of silver and air on a solution of the carbinol chloride. 15

The Carbinol Iodide.—A mixture of 1.000 g. of the carbinol chloride, 2.6 g. of silver and 30 cc. of benzene was rotated for 20 minutes. The mixture was then filtered, in an atmosphere of carbon dioxide, and titrated with a 0.1 N benzene solution of iodine. An equilibrium was established when 64% of the theoretical amount of iodine necessary to form the carbinol iodide had been added. A similar equilibrium has been found in the case of other triarylcarbinol iodides. That p-bromotriphenylcarbinol iodide had actually been formed was proved by the conversion of the reaction product into the chloride. Dry silver chloride was added and the mixture was shaken for several hours; p-bromotriphenylcarbinol chloride was isolated from the solution. $R_2C-I + AgCI = R_3C-CI + AgI$.

Although a number of attempts were made to isolate the radical of the first and that of the second order in a crystalline state none of the experiments led to the desired result. Both radicals seemed to be characterized by great solubility in all solvents except low-boiling petroleum ether; from the latter solvent, however, products were obtained that absorbed oxygen to only a small extent.

The Radicals from p-Bromodiphenyl-1-naphthylcarbinol Chloride.— In this set of experiments absolute ether was used as a solvent instead of

TABLE II

Removal of Carbinol Chlorine and Nuclear Bromine by Silver, and Estimation of the Capacity of the Resulting Radicals for Absorbing Oxygen

Calculated absorption for Radical of the First Order, 27.4 cc.; for Radical of the Second Order, 13.7 cc.

Time rotated Hours	Halogen removed Atoms Cl Br	Observed absorption of oxygen Cc., N. T. P.	Time rotated Hours	Halogen r Ato CI	emoved ms Br	Observed absorp- tion of oxygen Cc., N. T. P.
1/3	0.97 0.04	25.8	24	1.00	0.39	16.4
1/2	1.03 0.03	26.5	48	0.98	0.45	
1	0.96 0.12	24.5	72	0.96	0.48	13.2
$1^{1}/_{2}$	0.95 0.18		27 days	0.97	0.46	12.8
4	0.95 0.28	20.0	165 days	1.10	0.52	
12	1.08 0.31					

¹⁵ Gomberg, Ber., 37, 1635 (1904).

xylene and the tubes containing carbinol chloride, silver and solvent were treated as previously described.

The radical of the first order formed a deep violet solution, while that of the second order was an indigo color.

Peroxide of the Radical of the First Order; p-Bromodiphenyl-1-naphthylmethyl Peroxide, $[(Br_6CH_4)(C_6H_5)(C_{10}H_7)C]_2O_2$.—The deep violet solution of the radical, obtained by rotating 1.00 g. of the carbinol chloride, 3 g. of 20 mesh silver and absolute ether for 20 minutes, was quickly decolorized upon exposure to air. The yields of peroxide from two experiments were 0.87 g. and 0.84 g., or 91% and 88%, respectively. The peroxide, which is crystalline, is only slightly soluble in organic solvents and is colored deep green by coned. sulfuric acid. It melts with decomposition at 146°.

Analyses. Calc. for $C_{46}H_{32}O_2Br_2$: C, 71.15; H, 3.93; Br, 20.60. Found: C, 71.32; H, 4.02; Br, 19.77.

Peroxide of the Radical of the Second Order, $[(BrC_6H_4)(C_{10}H_7)(C_6H_5)C-C_6H_4-C(C_6H_5)(C_{10}H_7)]_2O_2$.—For the preparation of this substance a tube containing 1.00 g. of the carbinol chloride, 3 g. of 40-mesh silver and dry carbon disulfide was rotated for 60 hours. Upon exposure of the indigo-colored solution to the air it turned red and finally orange and, after the solvent had evaporated spontaneously, a yellow, resinous material remained. For purification, the peroxide was redissolved in a small amount of carbon disulfide and precipitated by the addition of a small amount of low-boiling petroleum ether; in this way a cream-colored, flocculent substance was obtained. It was found impossible to obtain the compound in crystalline condition. The peroxide, when heated, undergoes a gradual decomposition which begins at about 120°. It dissolves in carbon tetrachloride and benzene and is insoluble in alcohol, acetone or ethyl acetate.

Analysis. 16 Calc. C₉₂H₆₄O₂Br₂: C, 81.16; H, 4.74. Found: C, 80.96; H, 5.92.

Attempts to Isolate the Radicals.—The intensely colored solution, known to contain only the free radical of the first order, was siphoned into the apparatus designed for use in the isolation of free radicals.¹⁷ The solvent was removed at a low temperature under reduced pressure, and a gummy, indigo-blue residue was obtained. No spontaneous production of crystals could be obtained from a saturated solution of the radical; precipitating reagents likewise yielded only amorphous material. A solution of the amorphous substance absorbed a small amount of oxygen but complete decolorization did not take place.

Similar negative results were obtained in our attempts to isolate the radical of the second order.

The Radicals from Diphenyl-4-bromo-1-naphthylcarbinol Chloride.—A number of tubes, each containing 1.000 g. of the carbinol chloride, silver and solvent, were treated as previously described. In the tubes, used for the measurement of absorbed oxygen, bromobenzene was used, as before, for a solvent; for the silver halide determinations the carbinol chloride was dissolved in absolute ether.

¹⁶ The analytical results for bromine, obtained by the Carius method, were somewhat lower than those demanded by the above formula.

¹⁷ Gomberg and Cone, Ber., 37, 2033 (1904). Ref. 14, p. 1659.

TABLE III

Removal of Carbinol Chlorine and Nuclear Bromine by Silver and Estimation of the Capacity of the Resulting Radicals for Absorbing Oxygen

Calculated absorption for Radical of the First Order, 27.4 cc.; for Radical of the Second Order, 13.7 cc.

Time rotated	Halogen removed Atoms		Observed absorp- tion of oxygen	Time rotated	Halogen removed Atoms		Observed absorp- tion of oxygen	
Hours	CI	Br	Cc., N. T. P.	Hours	CI	\mathbf{Br}	Ce., N. T. P.	
$^{1}/_{3}$	0.93	0.00	25.6	12	1.01	0.35		
$^{1}/_{2}$	1.00	0.00	25.9	24	1.06	0.41	16.5	
1	1.09	0.11	24.3	48	1.06	0.51	14.0	
2	1.00	0.18		72	0.99	0.48	14.2	
4	1.08	0.27	20.5	27 days	0.98	0.49	14.0	

Peroxide of the Radical of the First Order, $[(C_6H_5)_2(BrC_{10}H_6)C]_2O_2$.—The ether solution of the radical was brown-red with a tinge of green. Exposure of the solution to the air resulted in an instant decolorization, accompanied by peroxide formation. The yield of peroxide obtained from 1 g. of the carbinol chloride was 0.82 g. or 86%. The peroxide is insoluble in cold benzene and when heated darkens at about 148° and melts with decomposition at 153–154°.

Analysis. Calc. for C46H32O2Br2: Br, 20.60. Found: 20.13

Peroxide of the Radical of the Second Order, $[(BrC_{10}H_7)(C_6H_5)_2C-C_{10}H_6-C-(C_6H_5)_2]_2O_2$.—The violet solution of the radical, obtained by rotating an ether solution of the carbinol chloride with silver for 48 hours, was decolorized at once upon exposure to air. The corresponding peroxide, which is quite soluble in ether, was precipitated to only a small extent; the bulk of the peroxide was obtained by allowing the solvent to evaporate spontaneously. This substance is a cream-colored, amorphous material and the color is changed to deep green by cone, sulfuric acid. In order to purify the substance for analysis it was dissolved in absolute ether and precipitated by the addition of low-boiling petroleum ether.

Analyses. Calc. for C₉:H₆₄O₂Br₂: C, 81.16; H, 4.74. Found: C, 80.81; H, 5.25.

When heated, the compound turned black at about 135° and gradually melted with decomposition.

Reaction between Silver Salts and the Carbinol Chlorides

p-Bromo-triphenylcarbinol Chloride and Silver Sulfate.—A number of sealed tubes, each containing 1.000 g. of the carbinol chloride, 3 g. of finely divided, thoroughly dried silver sulfate and 25 cc. of dry, acid-free nitrobenzene were prepared. Upon mixing the components a red solution was instantly formed. The tubes were rotated continuously, for a number of days, at a temperature of 50°.

After a definite period of reaction a tube was opened, the nitrobenzene solution filtered from the silver salts, and the amount of silver chloride and bromide in the latter was then estimated. The results of the silver halide analyses indicated to what extent the quinonoid sulfate (X) had been formed.

The highly colored, nitrobenzene solution was shaken with small amounts of 3% sodium hydroxide solution until the red color, due to the presence of the sulfate, had disappeared. Upon careful acidification of the alkaline extracts with acetic acid phydroxytriphenylcarbinol was obtained. The latter, after recrystallization from acetic acid, was isolated in the quinonoid modification.¹⁸

For further identification the colored carbinol was converted into the colorless, benzenoid form which was found to melt at 158–159°, as reported in the literature.

¹⁸ Gomberg, This Journal, **35**, 1036 (1913).

Finally, the benzyl derivative, prepared from the carbinol, was found to be identical with the benzyl compound previously described.¹⁹

In one experiment an analysis of the silver halides showed that, in addition to all of the carbinol chlorine, 74% of the nuclear bromine had been removed; the yield of phydroxytriphenylcarbinol obtained in this instance was 70%.

It was found inadvisable to allow the reaction between the silver and the brominated carbinol chloride to proceed to completion. When the mixture was rotated long enough to remove all of the nuclear bromine, a red, alkali-soluble oil resulted; this consisted, in part, of decomposition products of the sulfate; p-hydroxytriphenylcarbinol could not be isolated from the mixture. This latter fact is not surprising since even the pure, crystalline p-hydroxytriphenylcarbinol, in the quinonoid modification, decomposes through auto-oxidation when kept for some time in a stoppered bottle.

p-Bromodiphenyl-1-naphthylcarbinol Chloride and Silver Sulfate.—A mixture of 1.000 g. of the carbinol chloride, 3 g. of silver sulfate and 15 cc. of nitrobenzene was rotated, at 50°, for 3 days. The red-brown solution was then filtered and the nitrobenzene removed by distillation with steam. The red residue was dried, dissolved in a small amount of benzene and precipitated by the addition of petroleum ether. The precipitate was washed with low-boiling petroleum ether and finally recrystallized from alcohol. The yellow crystals which were obtained melted at $168-170^{\circ}$. This compound proved to be phenyl-1-naphthylquino-methane, 20 (C_6H_6)($C_{10}H_7$):C: C_6H_4 :O.

Diphenyl-4-bromo-1-naphthylcarbinol Chloride and Silver Sulfate.—Upon mixing 1.000 g. of the carbinol chloride, 3 g. of silver sulfate and 15 cc. of nitrobenzene a very deep green solution was instantly obtained. After rotation for 65 hours, at 50°, the solution had turned deep violet in color. The mixture was filtered and the solvent was removed by distillation with steam. The deep red, solid residue was shaken for 12 hours with a solution of 1.5 g. of sodium hydroxide in 50 cc. of 50% alcohol. After filtration the filtrate was acidified with acetic acid. The precipitated material was extracted with chloroform and the latter was then allowed to evaporate spontaneously. Upon treatment of the resulting residue with a small amount of acetic acid an orange-yellow, crystalline material was obtained. This compound melted at $178-179^\circ$ and was p-naphthofuchsone, $(C_6H_5)_2:C:C_10H_6:O$. When mixed with material prepared according to the literature, 21 the mixture melted at 179° .

In other series of experiments p-bromotriphenylcarbinol chloride in nitrobenzene solution was mixed with other silver salts, such as silver sulfite and silver nitrate. In each case intensely colored solutions resulted. Using silver sulfite a 68% yield of p-hydroxytriphenylcarbinol was obtained, thus proving that a quinonoid sulfite, entirely analogous to the sulfate, was formed as an intermediate product.

When silver nitrate was used, in the hope of obtaining a solution of the quinonoid nitrate, spontaneous decomposition of the resulting product took place, and only picric acid could be isolated.

This investigation was made with the assistance of The National Aniline and Chemical Company Fellowship. We wish to acknowledge our appreciation of the generous aid which has been given us.

Summary

- 1. p Bromodiphenyl 1 naphthylcarbinol, diphenyl 4 bromo 1 naphthylcarbinol and the corresponding chlorides have been synthesized and described.
 - 19 Gomberg and Buchler, This Journal, 45, 211 (1923).
 - ²⁰ Gomberg and Lang, *ibid.*, **42**, 1882 (1920).
 - ²¹ Gomberg and Sullivan, *ibid.*, 42, 1867 (1920).

p-Bromophenyl-chrysofluorene has been prepared and its constitution proved.

- 2. It has been shown that prolonged reaction between p-bromotriaryl-carbinol chlorides and excess of molecular silver, at ordinary temperature, results, in the first stage, in the removal of 1 atom of chlorine (carbinol chlorine); in the second stage, in the additional removal of $^{1}/_{2}$, and only $^{1}/_{2}$, of an atom of bromine (nuclear bromine). A formulation of the reaction has been given in this paper which explains not only the mobility of the nuclear bromine, but also gives a rational explanation of the removal of exactly $^{1}/_{2}$ of an atom, but no more, of the ring halogen. The explanation is based on the idea that the free radicals exist in 2 tautomeric modifications, benzenoid and quinonoid. According to this hypothesis, during the first stage of the reaction the radical of the "first order," R_3C \longrightarrow $R_2C = \bigcirc$ \longrightarrow H, results; during the second stage, a radical of the "second order," R_3C — C_6H_4 — CR_2 , is produced.
- 3. It was shown that the absorption of oxygen by the compound, formed by the removal of the carbinol chlorine alone, is equal in amount to that calculated for a free radical R_3C —. Furthermore, it has been demonstrated that the substance which results from the elimination of both the carbinol chlorine and $^{1}/_{2}$ of an atom of bromine absorbs only $^{1}/_{2}$ of the above quantity of oxygen, that is a quantity of oxygen demanded by the more complex radical of the "second order."

The peroxides corresponding to the two types of radicals have been isolated and analyzed.

- 4. Prolonged reaction between any of the 3 carbinol chlorides and silver sulfate results, likewise, in the removal of both carbinol and nuclear halogen. In this instance 1 atom, and not $^{1}/_{2}$ of an atom, of ring halogen was eliminated from 1 molecule of the triarylcarbinol chloride. This fact, also, is in complete harmony with the assumption that the bromine is a part of a quinonoid nucleus.
- 5. The general conclusion is that in the colored triarylmethyls, as well as in the colored, salt-like derivatives of the triarylcarbinols, color and quinoidation are concomitant phenomena.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, No. I, 27]
REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH
ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION. III.
THE REDUCTION OF NITROBENZENE BY SODIUM IN LIQUID
AMMONIA

By George F. White and Kenneth H. Knight Received March 3, 1923

It has been pointed out by Kraus and White¹ that organic compounds of very diverse function react with the alkali metals in liquid ammonia. The field offered for investigation is very extensive, since at present insufficient data are at hand to explain the mechanism of many new reactions and to predict the character of the products which might be formed. The selection of the reduction of nitrobenzene as a basis for the present study seemed very desirable in view of the general interest in the reduction of nitro compounds and, further, in view of the progress which would probably be made for the future investigation of the behavior under similar conditions of compounds of closely related function.

Both nitrobenzene and sodium are soluble in liquid ammonia, so that conditions in such a system are ideal for the rapid reduction of the nitro compound by the electrons of the highly ionized metal. Reduction in fact takes place extremely readily, and it is important to compare the process with the more familiar reductions in heterogeneous systems.

The reduction of nitrobenzene by sodium in non-aqueous media has to a certain extent been investigated. Hofmann and Geyger² found that sodium readily reacts with an ethereal solution of chloronitro-benzene and of chloronitro-toluene with the production of compounds in which sodium has entered the nitro group. They were unsuccessful in reducing nitrobenzene under similar conditions. Schmidt,³ however, was able to reduce nitrobenzene slowly in ethereal solution at ordinary temperature and rapidly in boiling toluene, that is, in the latter case, above the melting point of metallic sodium. He obtained a sodium compound to which he assigned the formula, $C_6H_5N(Na)ONa$, since it yielded β -phenylhydroxylamine when treated with acid. Schmidt also suggested the possibility that the disodium compound has the constitution $C_6H_5N(=O)Na_2$, and that it should thereby yield the hypothetical aniline oxide $C_6H_5N(=O)H_2$ with acids, aniline oxide then immediately rearranging to phenylhydroxylamine.

We have found that the same disodium derivative of phenylhydroxylamine as Schmidt obtained in toluene or ether solution is produced in

¹ (a) Kraus and White, This Journal, **45**, 768 (1923). See also (b) White, *ibid.*, **45**, 779 (1923).

² Hofmann and Geyger, Ber., 5, 915 (1872).

³ Schmidt, *ibid.*, **32**, 2911 (1899).

liquid ammonia by the reduction of nitrobenzene. The compound is rather insoluble in liquid ammonia, being precipitated as a red crystalline solid. Either sodium oxide is formed as a by-product and then is more or less completely ammonolyzed,4 or ammonia enters into the primary reaction with the formation of sodium amide and sodium hydroxide in equimolecular amounts. The reaction may then be expressed by the equation, $C_6H_5NO_2 + 4Na + NH_3 = C_6H_5N(Na)ONa + NaNH_2 +$ NaOH. By the addition of water to the reaction mixture azobenzene and azoxybenzene were isolated. However, these were substances produced by the secondary reactions of phenylhydroxylamine in hot alkaline aqueous solution. By the use of ammonium chloride in liquid ammonia the disodium salt was converted into its corresponding ammono acid in the absence of water. $C_6H_5N(Na)ONa + 2NH_4C1 = C_6H_5N(H)OH +$ $2\text{NaCl} + 2\text{NH}_3$. β -phenylhydroxylamine was extracted from the mixture with anhydrous solvents. In liquid ammonia, then, reduction of nitrobenzene proceeds as in all other solvents, phenylhydroxylamine being the first product to be isolated (or the sodium derivative of it), while nitrosobenzene may be assumed to be an intermediate product since indirect methods have indicated its formation in aqueous solutions. Azo bodies are not formed primarily but may result from secondary reactions in aqueous alkaline solution.

That disodium phenylhydroxylamine has the constitution, C₆H₅N(Na)-ONa, is very probable, since sodium would more readily add to oxygen than to nitrogen. Further, the compound reacts with alkyl halides in liquid ammonia, but no dialkylaniline oxide could be isolated from such reaction mixtures. It is of interest to note that preliminary experiments indicate that an excess of methyl iodide reacts with the sodium compound in liquid ammonia with the formation of an unstable oil. This oil has certain of the characteristics of the primary product which Bamberger and Tschirner⁵ obtained by the action of methyl iodide on dimethylaniline oxide and which they considered to be phenyldimethyl-methoxyammonium iodide, but which they found was too unstable to isolate. Such a compound could result from the disodium derivative of phenylhydroxylamine in liquid ammonia according to the following series: C₆H₅N(Na)ONa -> $C_6H_5N(CH_3)OCH_3 \longrightarrow C_6H_5N(I)(CH_3)_2OCH_3$. We have further shown that potassium amide reacts with phenylhydroxylamine in liquid ammonia. A red crystalline precipitate is produced which has the same physical properties as the sodium or potassium compound resulting from the reduction of nitro or nitrosobenzene. To test these views on the structure of the

⁴ Unpublished observations of E. F. Whyte in this Laboratory have proved that sodium oxide in liquid ammonia is rapidly ammonolyzed to sodium amide and sodium hydroxide.

⁵ Bamberger and Tschirner, Ber., 32, 1882 (1899).

disodium compound, a study of the formation of the alkyl derivatives of phenylhydroxylamine in liquid ammonia will be made.

Disodium phenylhydroxylamine is readily prepared by the reduction of nitrosobenzene in liquid ammonia: $C_6H_5NO + 2Na = C_6H_5N(Na)ONa$. As no by-products are formed, the reaction offers an especially good opportunity for further study of the structure of the sodium compound.

By the action of an excess of sodium in liquid ammonia, nitrobenzene is readily reduced to disodium anilide, which yields aniline by the action of ammonium chloride or water: $C_6H_5N(Na)ONa + 2Na + NH_3 = C_6H_5-NNa_2 + NaOH + NaNH_2$. Phenylhydroxylamine itself is reduced in liquid ammonia directly to aniline: $C_6H_5NHOH + 2Na + NH_3 = C_6H_5-NH_2 + NaOH + NaNH_2$.

A study of the reduction of azoxybenzene, azobenzene and hydrazobenzene in liquid ammonia has revealed the facts cited below.

Azoxybenzene is rapidly reduced to azobenzene: C_6H_5 —N—N— C_6H_5 +

 $2Na + NH_3 = C_6H_5 - N = N - C_6H_5 + NaNH_2 + NaOH$. By the further action of sodium on azobenzene, sodium atoms add directly to the azo group in the azobenzene molecule, whereby a disodium ammono salt of hydrazobenzene results: $C_6H_5 - N = N - C_6H_5 + 2Na = C_6H_5N(Na) - N(Na) - C_6H_5$. From this ammono salt hydrazobenzene may be obtained by the addition of ammonium salts of mineral acids or by the addition of water: $C_6H_5 - N(Na) - N(Na) - C_6H_5 + 2H_2O = C_6H_5 - N(H) - N(H) - C_6H_5 + 2NaOH$. The possible synthesis of quaternary hydrazines by the action of alkyl and aryl halides on the sodium salt of hydrazobenzene will be investigated.

The sodium derivative of hydrazobenzene is reduced by an excess of sodium to disodium anilide, C_6H_5 —N(Na)—N(Na)— C_6H_5 + 2Na = $2C_6H_5NNa_2$, from which compound aniline is obtained by the addition of water.

It is important to note in connection with these reductions that sodium does not react with free hydrazobenzene in liquid ammonia with the formation of the disodium derivative and the evolution of hydrogen, but that the molecule splits, and monosodium anilide is formed: C_6H_5 -NHNHC₆H₅ + 2Na = 2C₆H₅NHNa. The reduction of hydrazobenzene and of azobenzene to the mono- and disodium anilides, respectively, proceeds rapidly, and this method for the preparation of these latter compounds in liquid ammonia offers many advantages over the method of direct interaction of sodium and aniline.⁶

Considering the small quantities of reagents employed in the various experiments, good yields of phenylhydroxylamine, azobenzene and hydrazo-

⁶ Ref. 1b, p. 784. See also Picon, Compt. rend., 175, 1213 (1922).

benzene were obtained by the reduction of nitrobenzene, azoxybenzene and azobenzene, respectively. The method may prove of practical application in the synthesis of more valuable reduction products of other nitro and azo compounds.

Experimental Part

Apparatus and Procedure.—The apparatus and the experimental method employed were essentially identical with those described in the second article of this series.⁷

Materials.—The nitrobenzene used was redistilled thrice and had only a faint tinge of yellow color. Azoxybenzene, azobenzene and hydrazobenzene were obtained by reduction of nitrobenzene in alkaline aqueous solution, and β -phenylhydroxylamine by reduction of nitrobenzene in neutral solution in the usual manner. Nitrosobenzene was prepared by oxidation of phenylhydroxylamine. These nitrobenzene reduction products were recrystallized until pure as evidenced by their melting points.

The Reduction of Nitrobenzene

General Observations.—Franklin and Kraus⁸ have observed that the aromatic nitrohydrocarbons are more or less soluble in liquid ammonia, solutions of nitrobenzene being very little colored, but those of the polynitro compounds often being highly colored. Solutions of nitrobenzene showed no electrical conducting power, while those of dinitrobenzene evidenced a conductance which increased up to a maximum with time. Solutions of trinitrotoluene were found to attain their final conductance values at once.

In conformity with the above we have noted that nitrobenzene, which is very soluble in liquid ammonia, is colored red to violet in ammonia solution when only partially purified by distillation. Distillation of the compound three or four times gave a product which was colorless in ammonia solution. The impurities in the colored solutions were very probably traces of polynitro compounds which would act as pseudo acids, exhibiting the phenomena of "slow neutralization" observed by Franklin and Kraus and yielding colored ammonium salts of their aci forms. These observations substantiate the conclusions drawn from the following experiments, that nitrobenzene exhibits no desmotropic character in liquid ammonia solution and that no metallic derivatives of it are formed in such solutions.

As sodium was added in successive portions to colorless solutions of nitrobenzene in liquid ammonia, the solutions became yellow, then orange, dark red and finally dark brown, while a precipitate which at first appeared to be white darkened as the reduction proceeded. The color phenomena varied somewhat in the different experiments because minute amounts of certain of the colored reduction products had a marked effect on the appearance of the others. The reaction of the metal solution with the

⁷ Ref. 1b, p. 780.

⁸ Franklin and Kraus, Am. Chem. J., 20, 382 (1898); 23, 277 (1900).

nitro compound was rapid but was characterized by no excessive violence when the sodium was added in small portions. In the presence of a large excess of sodium, however, the reaction was very violent and explosions were apt to occur. On partial reduction of nitrobenzene, if the ammonia was then evaporated before addition of water and the reaction products exposed to the air, violent explosions resulted, accompanied by flame and the deposition of carbon.⁹

No hydrogen was evolved in any of the reductions.

When nitrobenzene was treated with sodium in the proportion of 1 molecule of the former to 1, 2 or 3 atoms of the latter, there was only partial reduction of the nitrobenzene, some of this substance being recovered from the mixture of reaction products.

The Formation of Disodium Phenylhydroxylamine.—Four and a half g. of sodium was added to a liquid ammonia solution of 6 g. of nitrobenzene, which corresponds to a ratio of 4 atoms of sodium to 1 molecule of the nitro compound. Before the last small portion of sodium was added the mixture was bright red in color but became dark brown on addition of the remainder; 11 g. of ammonium chloride was then introduced into the reaction tube and the mixture thoroughly stirred. All sodium compounds were thereby decomposed with the formation of insoluble sodium chloride. The resulting mixture was light yellow. The ammonia was evaporated and the dry residue extracted thrice with hot anhydrous benzene. The mixture was filtered and the benzene extract treated with an equal volume of anhydrous petroleum ether. After the solution had cooled, 1.9 g. of colorless crystals of β -phenylhydroxylamine (m. p., $80-82^{\circ}$) was obtained; yield, 36%. These were soluble in water, and the aqueous solution readily reduced ammoniacal silver nitrate and Fehling solutions.

The precursor of phenylhydroxylamine in the above experiment might be its disodium derivative, $C_6H_5N(Na)ONa$, or the disodium derivative of aniline oxide, $C_6H_5N(=O)Na_2$. In the latter case, aniline oxide, the hypothetical tautomer of phenylhydroxylamine, would, after being set free by addition of ammonium chloride, instantaneously rearrange into the hydroxylamine. It was found that the sodium reduction product reacted with methyl iodide in liquid ammonia with great readiness, but all attempts to isolate dimethylaniline oxide, $C_6H_5N(=O)(CH_3)_2$, were unsuccessful. On the other hand the following experiment indicates the formation of a dimethyl derivative of phenylhydroxylamine.

Three and six-tenths g. of nitrobenzene was reduced by 2.7 g. of sodium in liquid ammonia, whereby the disodium compound was produced; 16.8 g. of methyl iodide was then added, or twice as much as was required to form a dimethyl derivative of phenylhydroxylamine. The mixture was at first red but soon changed to a yellow color, and on the addition of 4 g. of ammonium chloride a clear yellow oil was formed which coagulated to an amorphous precipitate. After evaporation of the ammonia and extraction of the residue with ether, from the ether extract a reddish oil was isolated which when warmed had the odors of dimethylaniline and formaldehyde. These latter substances were likewise found by Bamberger and Tschirner⁵ to be formed when the unstable

 $^{^9}$ Schmidt, Ref. 3, has noted the explosive properties of disodium phenylhydroxylamine.

product of the reaction between dimethylaniline oxide and methyl iodide spontaneously decomposed.

Dipotassium Phenylhydroxylamine.—Several experiments proved that potassium reacts with nitrobenzene in liquid ammonia just as does sodium. A red, crystalline precipitate was formed and from this phenylhydroxylamine was prepared.

The following experiment confirms the assumed structure of the metallic compounds: 1.02 g. of potassium was dissolved in liquid ammonia and was converted into potassium amide by the catalytic action of ferric oxide; 1.5 g. of phenylhydroxylamine was then added. The colorless solution immediately became deep red in color and a red crystalline precipitate slowly separated. The following tentative reaction may be written: $C_6H_5N(H)OH + 2KNH_2 = C_6H_5N(K)OK + 2NH_3$.

Disodium Anilide.—One g. of nitrobenzene was reduced by 1.1 g. of sodium, that is, in the ratio of 1 molecule of the nitro compound to 6 atoms of sodium. The complete reduction was rather slow, and the mixture was allowed to stand for 24 hours. A brownish-green solution was obtained to which water was added. An oil, separated from this mixture, proved to be aniline.

The Formation of Sodium Amide.—To test for the formation of sodium amide in the reduction of nitrobenzene, 3.6 g. of nitrobenzene in liquid ammonia, was reduced by 2 g. of sodium, and then 9 g. of α -bromonaphthalene was added. Vigorous boiling of the liquid ammonia indicated that a reaction ensued. Water was then added, the ammonia evaporated, and the aqueous mixture acidified with hydrochloric acid. This mixture was extracted with ether to remove azoxybenzene and any unchanged bromonaphthalene, and the aqueous solution was then made alkaline. A small amount of α -naphthylamine separated from the solution. The synthesis of this compound in liquid ammonia may then be formulated thus: α -C₁₀H₇Br + NaNH₂ = α -C₁₀H₇NH₂ + NaBr.

The metal amide formed in the reduction of nitrobenzene in liquid ammonia does not react with any excess of the nitro compound. This was proved by a test experiment in which nitrobenzene was treated with potassium amide. The nitrobenzene was recovered unchanged.

The Secondary Formation of Azoxybenzene and Azobenzene

These compounds may be obtained when water is added to the mixtures of partially reduced nitrobenzene and liquid ammonia, and result from the familiar reactions of phenylhydroxylamine in alkaline aqueous solution.

Two g. of sodium was added to an ammonia solution of 3.6 g. of nitrobenzene. The final mixture was reddish-yellow. Water was added, the ammonia was evaporated, and the cooled aqueous solution filtered. The yellow residue was recrystallized from methyl alcohol; 1.8 g. of azoxybenzene, m. p. 34–36°, was obtained.

Two and eight-tenths g. of sodium was added to an ammonia solution of 3.6 g. of nitrobenzene. Water was added, and the insoluble residue obtained was twice crystallized from alcohol; 0.9 g. of azobenzene, m. p. 68.5°, was obtained.

The Oxidation of Disodium Phenylhydroxylamine

Three and six-tenths g. of nitrobenzene was reduced by 2.7 g. of sodium in liquid ammonia. Air was blown through the liquid ammonia mixture for $^3/_4$ hour. The color became very dark red; 6.4 g. of ammonium chloride was then added and a dark tarry mass separated. The ammonia was evaporated and anhydrous ether was added. The ether solution was green which would indicate the possibility of the presence of

some nitrosobenzene, although none of the compound was isolated. The ether extract yielded considerable nitrobenzene, but no phenylhydroxylamine. The experiment proved that disodium phenylhydroxylamine is oxidized to nitrobenzene in liquid ammonia.

The Reduction of Nitrosobenzene

Nitrosobenzene is insoluble in liquid ammonia. It was found to react with either potassium or sodium with great rapidity. A dark red solution was formed at first, but after 2 equivalents of the alkali metal were added a red crystalline precipitate slowly formed. This would indicate that the metallic derivatives of phenylhydroxylamine are to a certain extent soluble in liquid ammonia. Phenylhydroxylamine was isolated by the same procedure as described above in connection with the reduction of nitrobenzene.

The Reduction of Phenylhydroxylamine

Phenylhydroxylamine is extremely easily soluble in liquid ammonia. To a solution of 2 g. of this compound was added 0.84 g. of sodium. A light yellow precipitate (sodium amide and sodium hydroxide) formed, but no hydrogen was evolved in the reduction. The mixture became blue on the addition of 0.7 g. of sodium over the above amount, so that 2 atoms of sodium reacted with 1 molecule of the phenylhydroxylamine. The ammonia was evaporated leaving an oily residue from which aniline was extracted.

The Reduction of Azoxybenzene

Azoxybenzene is difficultly soluble in liquid ammonia, the solution being colored yellow; 4.3 g. of the substance was reduced by 1 g. of the sodium (1 molecule of azoxybenzene to 2 atoms of sodium). The reaction was very rapid, fine yellow crystals of azobenzene separating out of solution. These were isolated and crystallized from alcohol; yield, 77%; m. p., 63-68°.

The Reduction of Azobenzene

Formation of Hydrazobenzene.—Azobenzene dissolves to a slight extent in liquid ammonia with the production of a yellow solution; 3.95 g. of azobenzene was treated with 1 g. of sodium in liquid ammonia (in the ratio of 1 molecule of azobenzene to 2 atoms of sodium). The action was rapid and a blood-red solution was formed containing no precipitate. On addition of water a faintly yellow precipitate resulted. After evaporation of the ammonia the aqueous solution was filtered and the residue crystallized from alcohol. White crystals of hydrazobenzene were obtained; m. p., 126–129°; yield, 75%. No aniline was formed in the reduction.

Formation of Disodium Anilide.—One g. of azobenzene was reduced with 0.5 g. of sodium in ammonia (1 molecule of azobenzene to 4 atoms of sodium). A red-brown opaque solution resulted. Water was added and aniline was isolated from the aqueous solution. To test for the formation of disodium anilide in this reduction in liquid ammonia, 5.0 g. of azobenzene was treated with 2.5 g. of sodium, and 17.0 g. of ethyl iodide was then added to the liquid-ammonia solution. Water was then added and an ether extract of the aqueous solution yielded an oil that boiled at $205-215^{\circ}$ and evidently consisted mainly of diethylaniline. This substance was formed in ammonia by a reaction expressed by the equation, $C_6H_5NNa_2 + 2C_2H_5I = C_6H_5N(C_2H_5)_2 + 2NaI$.

The Reduction of Hydrazobenzene

Formation of Aniline.—Hydrazobenzene is readily soluble in liquid ammonia, yielding a pale yellow solution. When sodium was added to such a solution in the proportion of 1 molecule of hydrazo compound to 1 atom of sodium, the solution became dark red and a white gelatinous precipitate consisting probably of monosodium anilide (see below) was precipitated. No hydrogen was evolved in the reduction. After the addition

of water at least $^{1}/_{2}$ of the original amount of hydrazobenzene was recovered and some aniline was also obtained. The test showed that there was insufficient sodium for complete reduction and that the hydrogen atoms of the hydrazine molecule were not replaced by sodium.

Two g. of hydrazobenzene was treated with 0.5 g. of sodium in liquid ammonia (1 molecule of hydrazobenzene to 2 atoms of sodium). After the addition of water, by the usual procedure an oil was isolated which gave a violet color with sodium hypochlorite solution and boiled at 184° and, therefore, was practically pure aniline. No hydrazobenzene was recovered from the reaction mixture.

Formation of Monosodium Anilide.—Four g. of hydrazobenzene was treated with 1 g. of sodium as in the preceding experiment. To the mixture was then added 6.8 g. of ethyl iodide. Water was added and an ether extract of this aqueous solution yielded an oil which gave on distillation 2 fractions, one boiling at 185° consisting of aniline, and a second boiling at 200–205° consisting of mono-ethylaniline. The latter compound was synthesized in liquid ammonia evidently according to the following equation: $C_6H_5NH-Na + C_2H_5I = C_6H_5NHC_2H_5 + NaI$.

Summary

Nitrobenzene and nitrosobenzene are readily reduced by sodium in liquid ammonia with the formation of a disodium derivative of β -phenylhydroxylamine, the structural formula of which is probably $C_6H_6N(Na)$ -ONa. Phenylhydroxylamine is liberated from this salt in ammonia by the action of ammonium chloride, and the free phenylhydroxylamine may be isolated by extraction with anhydrous solvents after evaporation of the ammonia. By the further reduction of the disodium derivative in liquid ammonia, disodium anilide is formed and aniline is obtained from this by the action of ammonium chloride or water. Phenylhydroxylamine itself is reduced directly to aniline in liquid ammonia.

The disodium derivative of phenylhydroxylamine is oxidized in liquid ammonia to nitrobenzene by air.

Azoxybenzene and azobenzene are not formed as direct reduction products of nitrobenzene in liquid ammonia, but may be isolated after treatment of the partially reduced mixture with water. They result from the secondary reactions of phenylhydroxylamine in alkaline aqueous solution.

Azoxybenzene is reduced by sodium to azobenzene. Azobenzene is reduced to a disodium derivative of hydrazobenzene from which the latter compound may be obtained after treatment with ammonium chloride or water. The disodium derivative of hydrazobenzene may be further reduced by sodium in ammonia to disodium anilide, while hydrazobenzene itself is reduced by sodium to monosodium anilide.

Mono- and dialkylanilines may be synthesized in liquid ammonia by the action of alkyl halides on mono- and disodium anilides, respectively.

WORCESTER, MASSACHUSETTS

[Contribution from the Research Laboratories of the Dairy Division, United States Department of Agriculture]

THE QUANTITATIVE DETERMINATION OF TRYPTOPHAN

By George E. Holm and Geo. R. Greenbank

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Many methods, chiefly colorimetric, have been used for the quantitative determination of the tryptophan content of proteins, but few have given results accurate and concordant enough to warrant their general use where absolutely quantitative results are desired.

The bromine absorption test, the Adamkiewicz reaction, the nitroso-indole reaction, and others have been used with little real success.

Voisenet's¹ test for tryptophan, using formaldehyde in the presence of potassium nitrite and concd. hydrochloric acid, was made the basis for its quantitative determination by Fürth² and his associates, and excellent results were obtained. Their data indicate that the reaction of tryptophan with formaldehyde in the presence of sodium nitrite is rapid and while the color reaches a quite constant maximum, it may permit an error of from 10 to 20%. They also found that the color produced was very sensitive to an excess of hydrochloric acid, to excess of sodium nitrite and formaldehyde concentrations, to reducing and oxidizing substances and to metals. Various methods were tried for dissolving the proteins but the results obtained with these solutions are all within experimental error of the method.

The observation of Rhode,³ that tryptophan gives a blue color with p-dimethylaminobenzaldehyde, has found the most general application and has been used by Herz-feld,⁴ Kurchin,⁵ Thomas,⁶ and by May and Rose,⁷ While the methods employing this aldehyde are capable of very accurate results, the most general error in the method used by these workers has been due to the fact that the reactions in the standard or the unknown protein solutions have not been brought to a maximum color intensity.

The work of Gortner and Holm⁸ proved that the "humin" formed upon the acid hydrolysis of proteins in the presence of aldehydes was due to the presence of tryptophan. In the presence of a definite optimum amount of a certain aldehyde, the amount of "humin" formed, as measured by the nitrogen content, is a fairly accurate estimate of the amount of tryptophan. When a protein is allowed to stand at room temperature in the presence of benzaldehyde or some other aromatic aldehyde and 20% hydrochloric acid, a color develops which is peculiar to the aldehyde used. At lower temperatures this color is quite stable, but as soon as the solution is heated a dark "humin" is formed. The use of aliphatic aldehydes produces a dark condensation product immediately. Further unpublished work showed that the dark "humin" product formed when indole derivatives are condensed with aldehydes probably consists of a condensation of 1 molecule of the indole derivative with 2 or more molecules of the aldehyde. When the reaction is

¹ Voisenet, Bull. soc. chim., [3] 33, 1198 (1905).

² Fürth and Nobel, *Biochem. Z.*, 109, 103 (1920). Fürth and Lieben, *ibid.*, 109, 24 (1920).

³ Rhode, Z. physiol. Chem., 44, 161 (1905).

⁴ Herzfeld, Biochem. Z., 56, 256 (1915).

⁵ Kurchin, *ibid.*, **65**, 451 (1914).

⁶ Thomas, Ann. Inst. Pasteur, 34, 701 (1920).

⁷ May and Rose, J. Biol. Chem., 54, 213 (1922).

⁸ Gortner and Holm, This Journal, 39, 2485 (1917).

carried out in a molecular ratio of 1:1 the product is chiefly a soluble, deeply colored compound. These results indicate that if the reaction could be controlled, and if a reaction of a molecular ratio of 1:1 only could be obtained, the color produced would be a direct measure of the amount of an indole derivative present.

These observations emphasize the fact that in all cases where aldehydes are used care must be taken that conditions are such as to prevent the secondary reaction, as far as this can be done. The sensitiveness of the reaction used by Fürth and his associates is evident, since formaldehyde condenses very readily with tryptophan even at relatively low temperatures. The aldehyde used by Herzfeld, and by Thomas and more recently by May and Rose, p-dimethylaminobenzaldehyde, is very suitable, in that at lower temperatures very little or none of the secondary condensation products is formed. Herzfeld's error was evidently due to the fact that the reacting mixtures of either standards or unknowns were not allowed to

react long enough to produce a maximum color, and consequently his results are low in some cases. Thomas digested his proteins completely before applying the test and therefore his results are more nearly correct, although it is doubtful whether time enough was given for the development of maximum color. May and Rose used casein as a standard and calculated their results on the basis that the tryptophan content of casein is 1.50%, which is undoubtedly too

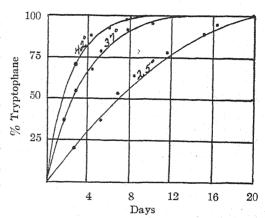


Fig. 1—Effect of temperature and time upon the rate of reaction of tryptophan with p-dimethylaminobenzaldehyde in 20% HCl

low. Figures given later will show that the time allowed for the completion of the reaction in their standards and the unknowns was too short.

Experimental Part

Herzfeld's method, slightly modified, has been used by the authors for some time, and has been found to be reliable when certain precautions are taken with regard to the conditions under which the determinations are made. It has also been applied to samples of proteins without previous digestion with enzymes, and reliable results have been obtained.

The effect of temperature and time upon the reactions involved when a pure sample of tryptophan is treated with p-dimethyl-aminobenzaldehyde in the presence of 20% hydrochloric acid is shown by the curves given in Fig 1.

At 25° the reaction is slow, but there is little danger of a great amount of the secondary condensation product forming at that temperature, as shown by the fact that in every case the reaction reaches completion though the time factor is very large. At 37° and 42° the reactions are much more rapid but do not show maximum color development until the sixth or eighth day in the case of the experiment at 42°, and not until the tenth or twelfth day in the case of the experiment at 37°. At 42° the color is not permanent for any length of time. Under these conditions, therefore, when working at about 37°, as did May and Rose, it is necessary to allow approximately 8 days for the standard to develop maximum color. Assuming that the color of their standard developed according to the curve in Fig. 1, it was approximately 70% developed. Inasmuch, however, as the color of the unknowns was proportionately developed, the results are good in most cases. As soon as maximum color has been developed in a standard or unknown, it is best maintained if the solution is kept at a temperature of 25° or lower and if, in addition, it is diluted. Under such conditions standards have been found to maintain their color for 8 or 10 days and in some cases even longer.

Some of the results obtained by applying the facts illustrated in Fig. 1 are shown in Table I.

Several 2 to 5 mg. samples of tryptophan were weighed out and each was placed in 100 cc. of 20% hydrochloric acid solution to which had been added an excess of the aldehyde. From time to time readings were made against standards by means of a Duboscq colorimeter, until the readings of the unknowns became constant.

Table I
RESULTS OBTAINED WITH PURE TRYPTOPHAN

	Expts.	Temperatures used ° C.	Calc. Mg.	ount of trypt Found Mg.	ophan——— Recovered
1.	(Av. of 5 detns.)	25, 37, one detn. at 42	5.00	4.985	99.7
2.	(Av. of 5 detns.)	25, 37, one detn. at 42	2.00	1.976	98.8
A		25	2.70	2.77	102.6
\mathbf{B}		25	1.20	1.17	97.5

A and B were samples of unknown concentration prepared by J. M. S.

The results obtained in these experiments indicate that pure tryptophane in solution can be accurately estimated by this method under the conditions given.

The effect of various concentrations of the aldehyde was determined and it was found that there was practically no difference in the rate of the reaction at 25° whether 1 mol. or 10 mols. of the aldehyde were used to each mol. of tryptophan. Two mols. seemed to give the best results.

For the determination of pure tryptophan in solution or in a mixture of amino acids the authors recommend the use of approximately 2 mols. of aldehyde to each mol. of tryptophan present. The reaction may be carried out at 25° or 37° . The latter is preferable.

The method has been tried upon proteins that have not been previously digested with enzymes. In these cases the method is dependent upon the rate of hydrolysis of the protein by the acid used, which is quite rapid in concd. acid solution and much slower in dil. acid. Inasmuch as the color is less stable in concd. than in dil. acid solution, it has been found that a 20% hydrochloric acid solution is most satisfactory. Sulfuric acid has not been tried.

Several samples of proteins were ground very fine and 0.10 g. of each was suspended in 100 cc. of 20% hydrochloric acid containing an excess of p-dimethyl-aminobenzaldehyde. Reactions were carried out at both 25° and 37°. Readings were made from time to time against standards containing 2 mg. and 5 mg. of pure tryptophan, using a Duboscq colorimeter, until the colors of the unknowns reached maximum intensity.

Results indicate that 37° is preferable to 25° in this experiment.

The results for casein, fibrin and Witte's peptone are embodied in Table II, which also gives results obtained by the same general method and by other methods. Some of the difficulties and errors of other authors who have used the same general method have been pointed out elsewhere in the paper.

Table II
Tryptophan Content of Casein, Fibrin and Witte's Peptone

		Folin and	Fürth and	May ⁷ and			Hopkins and
	Authors				Herzfeld ⁴	Thomas 6	
Casein	. 2.24	1.54	2.02	1.50	. 51	1.7-1.8	1.50
Fibrin from blood.	. 5.00	2.90	5.30		1.05	••••	
Witte's Peptone	5.40	3.03	5.30	••	1.25		• •

^a By formaldehyde-nitrite method.

With some proteins a sharp maximum in color intensity was produced, which extended over but 1 day. It is doubtful, therefore, whether results with all proteins are reliable when this method is used. This sharp maximum would indicate that a secondary reaction takes place to some extent before the primary color-producing reaction has been completed. The difficulty of hydrolysis of some proteins in the medium used may be a factor concerned here. From the results obtained upon pure tryptophan it seems that in general the best results might be obtained with the use of samples of proteins previously digested by enzymes.

In this connection it is interesting to call attention to the tryptophan content of fibrin as determined by Gortner and Holm.⁸ The fibrin used in the determinations reported in this paper was taken from the same sample as that used in their work upon "humin." formation. They estimated that in the presence of an optimum amount of formaldehyde 95% of the tryptophan was removed as "humin." Their figures indicate that

⁹ By phenol regent method. Folin and Looney, J. Biol. Chem., 51, 421 (1922).

¹⁰ By direct isolation, Hopkins and Cole, J. Physiol., 27, 418 (1901-2).

the tryptophan content of this fibrin, calculated upon the basis of the humin nitrogen was 4.8%. The total tryptophan content would therefore be 5.05% which is in excellent agreement with the value obtained by the colorimetric method.

Summary

- 1. Some of the difficulties and errors in the methods used by various authors are pointed out.
- 2. The effect of temperature and time upon the reaction of p-dimethylaminobenzaldehyde in 20% hydrochloric acid has been studied. In this concentration of hydrochloric acid the reaction requires greater time for completion than is generally supposed. The higher the temperature, the greater the instability of the color produced.
- 3. Pure tryptophan in solution can be accurately determined by use of this method. The tryptophan content of proteins can also be accurately determined without previous hydrolysis of the protein, but from observations and from general considerations it seems that an enzyme-digested protein is better suited for this determination than is undigested protein.
- 4. There is excellent agreement between the figures for the tryptophan content of fibrin obtained by the "humin" formation method of Gortner and Holm⁸ and those obtained by the colorimetric method.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF H. A. METZ]

SOME NEW DERIVATIVES OF SYNTHETIC ADRENALINE (SUPRARENINE)

By Casimir Funk and Louis Freedman Received March 23, 1923

In the manufacture of synthetic adrenaline, and especially in its purification, we have observed the formation of certain derivatives which are of unusual chemical interest, and which may prove to have valuable pharmacological properties.

It has been found that the secondary alcohol group in the side chain

forms ethers of the type HO —CH(O—R)—CH₂NHCH₃, where R represents an alkyl radical. A derivative of adrenaline has been prepared by Mannich¹ in which the hydrogens of all 3 hydroxyl groups have been replaced by methyl groups, but so far as we are aware no derivatives have as yet been described in which only the secondary alcohol group has been converted into an ether.

We have succeeded in preparing the methyl and ethyl ethers of this type, but have failed so far to prepare the purified propyl and benzyl

¹ Mannich, Arch. Pharm., 248, 127, 154 (1910).

derivatives. Large amounts of tarry residue, from which it is difficult to obtain the pure products, are formed with the higher homologs.

These new ethereal compounds differ from adrenaline in that they form soluble and easily oxidizable bases and, therefore, have to be isolated and purified as the hydrochlorides. We have as yet been unable to reconvert these ethers into adrenaline by hydrolysis; vigorous hydrolysis cannot be used because of the ease with which these compounds decompose.

In the preparations of the ethyl compound, when the reaction to form the ether is made more vigorous, another new compound, which has also been isolated and purified, is formed. This compound is probably the dihydrochloride of the di-ether of adrenaline with the structure

of water from 2 molecules of adrenaline.

None of the above compound was formed as a by-product in the preparation of the methyl ether, even though the reaction was carried out under higher temperature and pressure. Further work on the preparation of these compounds, and their pharmacologic action, is now being carried out.

Experimental Part

Preparation of the Hydrochloride of the Ethyl Ether of r-Adrenaline, r-3,4-Dihydroxy-phenyl Ethyl-ethanol-methyl Amine Hydrochloride.—Racemic adrenaline (synthetic) was heated with absolute ethyl alcohol containing various amounts of dry hydrogen chloride for various periods of time. We will describe only those experiments that gave the best results.

A solution of 4.4 g. (0.02 mole) of adrenaline hydrochloride in 44 cc. of absolute ethyl alcohol containing 0.02 mole of dry hydrogen chloride was refluxed for 1 hour on a waterbath. It was then filtered, the filtrate evaporated to half volume and the residue allowed to stand over sulfuric acid. On the next day, a crop of crystals was obtained which when filtered and washed with absolute alcohol, and dried, gave 2.4 g. of a white crystalline compound melting at 163° (with decomposition). After recrystallization from absolute alcohol, the material weighed 2.0 g. and melted at $165-166^{\circ}$. After 4 recrystallizations from absolute alcohol it melted at 169° (corr.); r-adrenaline hydrochloride melts at 157° . This new compound is soluble in 2.5 parts of absolute alcohol. It is readily soluble in water and its aqueous solution, on addition of ammonia, yields a soluble base which oxidizes very quickly in the presence of an excess of ammonia. The highest yield of the ethyl ether was obtained by using 1.5 molecular equivalents of hydrogen chloride and refluxing for $^{1}/_{2}$ hour. Thus, from 22 g. of adrenaline hydrochloride, we obtained 16 g. (65%) yield) of the hydrochloride of the ether.

In its color reactions it resembles adrenaline. With ferric chloride, it gives a dark green which turns to a maroon-red on standing or on addition of ammonia. It also gives an orange-red to a bright red color on addition of mercuric chloride and sodium acetate to its aqueous solution. These color reactions prove that the phenolic groups

in the ring are free, and that the secondary alcohol group can still give the sublimate reaction, even though the alcohol group is converted to an ether. On treatment with sodium nitrite in hydrochloric acid solution, the compound gives a yellow oil which shows the characteristic Lieberman nitrosamine reaction, proving the presence of a secondary amine and precluding the possibility of the addition of the ethyl group on the nitrogen.

Analyses.² Subs., 0.2788: 11.5 cc. of 0.1 N HCl. Subs., 0.0971: Cl, 0.0138; CO₂, 0.1212; H₂O, 0.0642. Calc. for $C_{11}H_{15}O_{5}NCl$: C, 53.36; H, 7.32; N, 5.65; Cl, 14.35. Found: C, 53.60; H, 7.34; N, 5.73; Cl, 14.21.

The hydrogen chloride can also be titrated directly with standard alkali, the formation of the easily oxidizable base giving a red color in excess alkali, thus acting as an indicator.

Preparation of Di-adrenaline-ether Dihydrochloride.—A solution of 45 g. of racemic adrenaline hydrochloride in 450 cc. of absolute ethyl alcohol containing 36.5 g. of dry hydrogen chloride (4 molecular equivalents) was refluxed for 1 hour. The product failed to crystallize at first, but after it had stood over sulfuric acid for several days a crop of crystals weighing 20 g. was obtained. This substance did not melt sharply and appeared to be a mixture. The bulk of it was practically insoluble in absolute alcohol, but was recrystallized from 70% alcohol, the more soluble ethyl ether hydrochloride remaining in solution while the di-adrenaline-ether dihydrochloride crystallized in clusters of thin rectangular prisms. The compound melted at $166-174^{\circ}$ without decomposition, forming a yellow oil. It was triturated in a mortar with 95% alcohol, filtered and washed several times with 95% alcohol; m. p., $172-180^{\circ}$. On further recrystallizing and washing, the compound melted sharply at $180-183^{\circ}$. The final yield of the pure product was 3 g., the remaining material being the ethyl ether described in the previous experiments.

Color Reactions.—With ferric chloride it gives a deep green which passes to a reddishviolet and then to a violet on standing or on addition of ammonia. With mercuric chloride and sodium acetate, it gives a grayish-blue precipitate which darkens on standing. With ammonia alone it forms a gray precipitate which dissolves in an excess of ammonia, giving a purple solution. It is precipitated by phosphotungstic and phosphomolybdic acids, forming a grayish-white precipitate. The ethyl and methyl ethers are not precipitated by these reagents.

Analyses. Subs., 0.2779: 13.8 cc. of 0.1 N HCl. Subs., 0.1185: CO₂, 0.2243; H₂O, 0.0678; Cl, 0.0199. Calc. for $C_{15}H_{26}O_{5}N_{2}Cl_{2}$: C, 51.29; H, 6.22; N, 6.68; Cl, 16.83. Found: C, 51.67; H, 6.35; N, 6.8; Cl, 16.87.

Preparation of the Hydrochloride of Methyl Ether of Racemic Adrenaline. (r-3,4-Dihydroxy-phenyl-methyl-ethanol-methylamine Hydrochloride.)—A solution of 11 g. of racemic adrenaline hydrochloride in 110 cc. of absolute methyl alcohol containing 7.3 g. (4 molecular equivalents) of dry hydrogen chloride was refluxed for 1 hour. The methyl ether crystallized immediately as the reaction mixture cooled, forming thin rectangular prisms. The crude compound melts at 172–173° with effervescence. It is very soluble in absolute methyl alcohol but less soluble in absolute ethyl alcohol. On recrystallization from 5 parts of absolute ethyl alcohol, it separated in white rectangular prisms similar to the ethyl derivative; m. p., 175° (corr.); yield, 3 g. or about 26%. This methyl ether gives the same color reactions as does the ethyl derivative.

Analyses. Subs., 0.2536: 10.7 cc. of 0.1 N HCl. Subs., 0.0978: CO₂, 0.1863; $\rm H_2O$, 0.0630; Cl, 0.0150. Calc. for $\rm C_{10}H_{16}O_2NCl$: C, 51.37; H, 6.90; N, 5.99; Cl, 15.18. Found: C, 51.94; H, 7.15; N, 5.95; Cl, 15.33.

An attempt to form the di-adrenaline ether by means of this reaction, even by heating at higher temperatures in a sealed tube, failed. Only the methyl ether was obtained.

² All combustions were made by the Dennstedt method.

Summary

Racemic adrenaline hydrochloride is readily converted into ethers in which the hydrogen of the secondary alcohol group is replaced by an alkyl group, by treating it with the corresponding absolute alcohol containing dry hydrogen chloride. The methyl and ethyl ethers have thus far been obtained and described. In the formation of the ethyl ether we have isolated as a by-product what appears to be di-adrenaline ether, formed by the condensation of 2 molecules of adrenaline with the elimination of 1 molecule of water from the 2 secondary alcohol groups.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE ACTION OF SELENIUM OXYCHLORIDE UPON ETHYLENE, PROPYLENE, BUTYLENE AND AMYLENE¹

By Carl, E. Frick Received April 20, 1923

Preliminary experiments by Lenher² have shown that the oxychloride of selenium reacts with saturated paraffin hydrocarbons only very slowly at high temperatures, while with the unsaturated hydrocarbons of the aliphatic series, it unites directly, frequently with great evolution of heat. Mueller³ has reported that selenium oxychloride reacts with unsaturated hydrocarbons and ketones, producing substances that are very unstable in light and air. He gave no analytical results, however, nor any properties of the substances produced. The object of this investigation has been to make a quantitative study of the reactions taking place between selenium oxychloride and the olefins, ethylene, propylene, butylene and amylene; and to compare these reactions with those of selenium monochloride and the same olefins.

When selenium oxychloride reacts with ethylene, the dichloride of bis $(\beta$ -chloro-ethyl)selenide is always produced, regardless of whether the ethylene or the oxychloride is in excess during the course of the reaction. With selenium monochloride and ethylene, Boord and Cope⁴ have pointed out that this reaction takes place in two stages and that bis $(\beta$ -chloro-ethyl)selenide is produced when the ethylene is in excess, while the dichloride of bis $(\beta$ -chloro-ethyl)selenide is always formed when the monochloride is in excess.

¹ This paper is constructed from a part of a thesis submitted by the author to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, January, 1923.

² Lenher, This Journal, 43, 29 (1921).

³ Mueller, Chem.-Ztg., 43, 843 (1919).

⁴ Boord and Cope, This Journal, 44, 395 (1922).

Preparation of Materials

Selenium Oxychloride.—The method of Lenher⁵ was used, which consists in the union of selenium tetrachloride and selenium dioxide in a medium of carbon tetrachloride. The oxychloride was freed from carbon tetrachloride by fractionation and purified further by two distillations under reduced pressure.

The Olefins.—Ethylene and propylene were made by the method of Newth, 6 which consists in the dehydration of the corresponding alcohols with glacial phosphoric acid. isoPropyl alcohol was used in the preparation of the propylene. The best yields were obtained when the phosphoric acid was kept at a temperature of 210° in the case of the preparation of ethylene and at 360° in the case of the preparation of propylene. β -Butylene was prepared from N-butyl alcohol by the contact method of King. The catalyst used was pumice stone impregnated with glacial phosphoric acid. Temperatures from 280–400° gave practically the same yields of β -butylene. The γ -butylene was removed by bubbling the gaseous product through 60% sulfuric acid. The amylene was a commercial sample and was purified by the method improved and successfully used in connection with the course in Organic Chemical Manufacturing at the University of Illinois. This method worked very well and gave practically pure trimethylethylene, boiling at 36–38°. The yield was about 350 cc. per liter of crude amylene.

Experimental Part

In order to find out whether the same products were obtained in the interaction of selenium oxychloride and the olefins when the selenium oxychloride was added in excess, and when the olefin was in excess, two general procedures were used.

- 1. The olefin was passed into pure selenium oxychloride or a solution of it in an inert solvent, usually chloroform, until absorption of the olefin was completed. The reaction proceeded with evolution of heat and sometimes required cooling. When no more olefin was absorbed, the solvent was evaporated under diminished pressure, and the crude material was purified by crystallization from a suitable solvent. When a liquid product was obtained that could not be crystallized it was purified by fractional distillation under diminished pressure.
- 2. The selenium oxychloride in an inert solvent, usually chloroform, was dropped into an atmosphere of the olefin, in such a way that the latter was always maintained in excess throughout the course of the experiment. A 3-liter, Pyrex flask served as the reaction chamber and was fitted with a mercury-sealed glass stirrer, a dropping funnel, and an inlet and outlet tube for the olefin. The olefin was passed in until the air was displaced and the solvent saturated. The selenium oxychloride solution was then permitted to drop from the funnel at such a rate that the olefin was always maintained in excess. The reaction took place slowly, the walls of the flask becoming coated with selenium dioxide. After the
 - ⁵ Lenher, This Journal, 42, 2498 (1920).
 - ⁶ Newth, J. Chem. Soc., 79, 915 (1901).
 - ⁷ King, ibid., 115, 1401 (1919).
- 8 Adams, Kamm and Marvel, "Organic Chemical Reagents," John Wiley and Sons. 1919.

addition of a measured quantity of the oxychloride solution, the agitation was continued for a few minutes in the presence of the olefin and the operation interrupted. The reaction mixture was filtered rapidly by suction and the solvent evaporated under reduced pressure. The crude, oily product was purified by crystallizations from a suitable solvent or by fractional distillation under diminished pressure, as the nature of the product required.

Bis(β -chloro-ethyl)selenide Dichloride.—(1) Dry ethylene was passed into a solution of 83 g. (1 /2 mole) of selenium oxychloride dissolved in 200 cc. of anhydrous chloroform, until no more was absorbed. The ethylene was rapidly absorbed with evolution of heat, and a white, crystalline substance separated, clogging the inlet tube from time to time. The solution remained practically colorless; no reduction to selenium monochloride took place. (2) Two hundred cc. of a solution of selenium oxychloride in anhydrous chloroform, containing 85 g. of pure selenium oxychloride, was dropped slowly into an atmosphere of ethylene. A white, crystalline substance separated but more slowly than when the oxychloride was in excess.

The reaction mixtures were freed from the solvents by evaporation, the crude products purified by repeated crystallizations from chloroform or carbon tetrachloride, and dried at room temperature. Bis(β -chloro-ethyl)selenide dichloride was obtained in both cases, as long, white, prismatic crystals; m. p., 121.5°.

The product was analyzed for selenium by fusion of $0.2~\rm g$. of substance with 8–10 g. of a 1:1 mixture of anhydrous sodium carbonate and sodium peroxide. After fusion, the melt was dissolved with water, the solution acidified with hydrochloric acid and filtered. An excess of hydrochloric acid, sufficient to bring the concentration of the solution to $15~\rm to~20\%$ of hydrochloric acid, was added and the selenium precipitated from the hot solution by $25~\rm cc.$ of a saturated solution of sulfur dioxide. Chlorine was determined either by fusion in a similar manner, acidifying with nitric acid and titrating by the Volhard method, or by Stepanoff's³ absolute alcohol-sodium method.

Analyses. Calc. for $C_4H_8Cl_4Se$: C, 17.33; H, 2.91; Cl, 51.05; Se, 28.58. Found: C, 17.08, 16.97, 17.13; H, 2.91, 3.07, 3.30; Cl, 51.22, 51.49, 51.05; Se, 28.80, 28.45, 28.50.

When the crystals were dissolved in cold water it was found that partial hydrolysis had taken place. When a little nitric acid was added and the chlorine precipitated in the cold by silver nitrate, exactly $\frac{1}{2}$ of the total chlorine was precipitated.

Analysis. Total chlorine: 51.15. After hydrolysis in cold water only: 25.56.

This compound was first described by Heath and Semon, 10 who obtained it by passing ethylene into a solution of selenium monochloride. Their sample melted at 118° , and after they had made several analyses they came to the conclusion that it was symmetrical tetrachloro-diethyl selenide. About the same time, Bauser, Gibson and Pope, 11 making use of the same reaction, obtained a white, crystalline compound, slightly hygroscopic, melting at 122.5° . They showed by analysis that the compound was β - β '-dichloro-diethyl selenide dichloride, and that upon reducing this substance in water solution with sulfur dioxide, they obtained β - β '-dichloro-diethyl selenide as a colorless oil that solidified when cooled.

Because of this apparent disagreement in the results of these different workers, selenium monochloride was prepared by the method of Divers and Shimose, 12 and the reaction with ethylene duplicated. When ethylene was passed into the solution of

Stepanoff, This Journal, 38, 711 (1916).

¹⁰ Heath and Semon, J. Ind. Eng. Chem., 12, 1101 (1920).

¹¹ Bauser, Gibson and Pope, J. Chem. Soc., 117, 1453 (1920).

¹² Divers and Shimose, *ibid.*, **45**, 198 (1884).

selenium monochloride in benzene, red selenium separated and a white substance crystallized. After purification by crystallization from benzene, the product was shown by analysis as well as by its melting point to be identical with the product obtained from ethylene and selenium oxychloride, which has been shown to be $bis(\beta$ -chloro-ethyl)-selenide dichloride.

Bis $(\beta$ -chloropropyl) selenide Dichloride.—(1) Dry propylene gas was passed into a solution of 85 g. of pure selenium oxychloride until absorption was completed. The propylene was rapidly absorbed with evolution of heat. A white, crystalline substance separated at once. (2) A solution of about 40 g. of selenium oxychloride in 183 cc. of anhydrous chloroform was allowed to drop slowly into an atmosphere of propylene. A white, crystalline solid settled in this case also.

The reaction mixtures were freed from the solvents by evaporation, the solid products purified by repeated crystallizations from petroleum ether, and dried at room temperature. Bis(β -chloropropyl)selenide dichloride was obtained in both cases as white, plate-like crystals resembling naphthalene, melting at 80°.

Analyses. Calc. for $C_6H_{12}Cl_4Se$: C, 23.60; H, 3.96; Cl, 46.48; Se, 25.95. Found: C, 23.43; H, 3.98; Cl, 46.43; Se, 25.67.

This compound has been prepared by Boord and Cope⁴ by passing propylene gas into an excess of selenium monochloride dissolved in benzene. They describe it as a white, crystalline compound melting at 81°.

Bis $(\beta$ -chlorobutyl) selenide Dichloride.—In an attempt to isolate bis $(\beta$ -chlorobutyl)-selenide dichloride, (1) dry β -butylene was passed into 85 g. of pure selenium oxychloride until absorption was completed. The butylene was rapidly absorbed with evolution of heat. A yellowish, viscous mass was obtained which was stable as long as the mixture was kept cooled in ice water. When the product was allowed to come to room temperature, red selenium separated and a dark, oily product remained. (2) A solution of 42 g. of selenium oxychloride in 183 cc. of anhydrous chloroform was dropped slowly into an atmosphere of β -butylene. A white, crystalline substance separated slowly (identified as selenium dioxide), and the solution became reddish-yellow. The chloroform was evaporated under reduced pressure and an oily substance remained. This crude product could not be induced to crystallize. It was decomposed by distillation even under strongly reduced pressure.

In several experiments, a small, dark red fraction was obtained, boiling at 104-108° under 68 mm. pressure.

Analyses. Calc. for $C_8H_{16}Cl_4Se$: Cl, 42.57; Se, 23.74. Calc. for $C_8H_{16}Cl_3Se$: Cl, 35.86; Se, 26.69. Found: Cl, 37.00, 37.08; Se, 26.70, 26.46.

The selenium content of this small fraction is near that required for the unsymmetrical β - β '-dichlorobutyl- β '-chlorobutyl selenide. It is improbable that this compound is one of the main products of the reaction; rather, it is present only in small amounts among the decomposition products. It is believed from observations made throughout the course of the reaction, that the dichloride of bis(β -chlorobutyl)selenide was formed whenever the temperature of the reaction mixture was kept below 10°. The formation of the same by-product, selenium dioxide, showed that the reaction proceeded in a manner similar to that of the reactions of ethylene and propylene with selenium oxychloride.

Boord and Cope⁴ were also unable to obtain the dichloride of $bis(\beta-chlorobutyl)$ selenide when using selenium monochloride and butylene.

Bis(β -chloro-amyl)selenide Dichloride.—In an attempt to prepare bis(β -chloro-amyl)selenide dichloride, (1) 35 g. (0.5 mole) of amylene dissolved in 200 cc. of anhydrous chloroform was added gradually to 83 g. (0.5 mole) of selenium oxychloride dissolved in 200 cc. of anhydrous chloroform. As soon as the two solutions were brought

together, selenium dioxide separated. After the reaction mixture had stood for 24 hours in a refrigerator, it was filtered and the chloroform evaporated under diminished pressure. (2) A solution of 83 g. (0.5 mole) of selenium oxychloride in one series of experiments, and 41.5 g. (0.25 mole) of selenium oxychloride in another series of experiments, each dissolved in 150 cc. of anhydrous chloroform, was allowed to drop slowly into 35 g. (0.5 mole) of amylene dissolved in 200 cc. of anhydrous chloroform and cooled to 0° in an ice-bath. Selenium dioxide separated at once, and after all of the selenium oxychloride solution had been added the selenium dioxide was separated and the chloroform evaporated under reduced pressure.

The crude products in each case did not crystallize, but underwent decomposition even under greatly reduced pressure. Selenium monochloride was identified as one of the liquid fractions, and there was obtained a small quantity of a pale yellow, almost colorless liquid; b. p., $85-100^{\circ}$ (atm.). The product was doubtless a mixture of amyl chlorides. Pure tertiary amyl chloride boils at 86° .

Analyses. Calc. for $C_{10}H_{20}Cl_4Se$: Cl, 39.29; Se, 21.92. Calc. for $C_5H_{11}Cl$: Cl, 33.28. Found: Cl, 33.40, 33.19; Se, none.

It is believed that the reaction proceeded in a manner similar to that of ethylene and propylene with selenium oxychloride, and that the dichloride of bis(β -chloro-amyl)-selenide was formed whenever the reaction mixture was kept below 10°. Selenium dioxide was identified as a by-product.

Boord and Cope⁴ were also unable to obtain the dichloride of $bis(\beta$ -chloro-amyl)-selenide, when using selenium monochloride and amylene.

Discussion of Results

These results show clearly that when selenium oxychloride reacts with the olefin hydrocarbons, the dichlorides of the corresponding alkyl selenides, are always produced regardless of whether the olefin or the oxychloride are in excess during the course of the reaction. Selenium dioxide has been identified as the by-product in every case, and since no selenium monochloride or selenium is produced, the reaction may be expressed as follows: $2C_nH_{2n} + 2Cl_2SeO = (Cl C_nH_{2n})_2Se Cl_2 + SeO_2$.

It is interesting to compare the above equation with the one given by Boord and Cope⁴ for the interaction of selenium monochloride and the oelfins when the selenium monochloride is in excess: $2 C_n H_{2n} + 2 Cl_2 Se = Se = (ClC_n H_{2n})_2 SeCl_2 + 3 Se$. Boord and Cope give the mechanism of this latter reaction as evidence in favor of the unsymmetrical structure for selenium monochloride. The similarity of the two preceding equations as written, and the results obtained in the syntheses described in this paper, are offered as still further evidence of the correctness of the unsymmetrical formula for selenium monochloride. Boord and Cope have given the credit for the suggestion of this formula to Konek-Norwall¹³ but it appears that Divers and Shimose, ¹⁴ nearly 30 years earlier, gave its formula as $Se = SeCl_2$, and to them, therefore, should be given the credit for suggesting this unsymmetrical structure.

¹³ Konek-Norwall, Oesterr. Chem. Ztg., 16, 288 (1913).

¹⁴ Ref. 12, p. 194.

The author wishes to express his appreciation to Professor Victor Lenher, at whose suggestion and under whose direction this work was carried out.

Summary

- 1. The reactions between selenium oxychloride and ethylene, propylene, butylene and amylene have been studied.
- 2. The mechanism of the reaction between selenium oxychloride and the olefins has been formulated and has been compared with that of selenium monochloride and the olefins.
- 3. It has been shown that with selenium oxychloride and the olefins, the dichlorides of the corresponding alkyl selenides are always formed regardless of whether the oxychloride or the olefin is in excess during the course of the reaction.
- 4. It has been shown that the final reaction products of selenium monochloride and the olefins are identical with those formed by the interaction of selenium oxychloride and the olefins.
- 5. The results obtained in these syntheses have been offered as further evidence in favor of the unsymmetrical structure for selenium monochloride.

Madison, Wisconsin

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE ACTION OF SELENIUM OXYCHLORIDE ON PURE RUBBER 1

By CARL E. FRICK Received April 20, 1923

In the studies on the oxychloride of selenium which have been in progress in this Laboratory, Lenher² has shown that pure rubber, vulcanized rubber and vulcanite react chemically with selenium oxychloride. It seemed advisable to undertake a quantitative study of this reaction, if possible, as any information would be interesting in view of our incomplete knowledge of the nature of the rubber hydrocarbon. The products obtained by the action of selenium oxychloride on 2 wild, and 2 plantation rubbers, and a synthetic rubber prepared from isoprene, were investigated.

Preparation of Materials

Selenium Oxychloride.—The method of Lenher³ was used.

Pure Rubber Hydrocarbon.—Samples4 of crude, unworked rubber were washed

¹ This paper is constructed from a part of a thesis submitted by the author to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, January, 1923.

² Lenher, This Journal, 43, 29 (1921).

³ Lenher, ibid., 42, 2498 (1920).

⁴ These samples were kindly furnished by Dr. W. C. Geer of the B. F. Goodrich Co. and Prof. H. E. Simmons of the University of Akron.

in frequent changes of water until dirt and soluble impurities were removed, dried, and freed from resins by extraction with boiling acetone for 24 hours. The residue was freed from acetone and the rubber hydrocarbon dissolved in pure carbon tetrachloride. The undissolved protein was filtered off and the rubber precipitated by absolute alcohol. The sample was freed from alcohol, redissolved in carbon tetrachloride, reprecipitated by alcohol 7 times, and finally redissolved and kept in pure carbon tetrachloride. The following natural rubbers were used in this study: Upriver, fine, hard Para; first latex Pale Crepe; Upper Caucho Ball; and ribbed Smoked Sheet.

Synthetic "Isoprene Rubber."—This was prepared from pure isoprene by the well-known method discovered practically simultaneously by Mathews⁵ in England and Harries⁶ in Germany, using metallic sodium to effect the polymerization. The rubbery mass was washed with acetone, dissolved in carbon tetrachloride, reprecipitated by alcohol, redissolved and reprecipitated several times, and thus purified in exactly the same manner as the natural rubbers. The sample was finally redissolved and kept in pure carbon tetrachloride.

Isoprene.—The isoprene was prepared from dl-limonene (dipentene) by passing the vapors over an electrically-heated platinum wire, using the principle of Harries' isoprene lamp. The limonene was obtained from washed orange oil, which was over 96% pure limonene. The crude isoprene was freed from any contained amylene by allowing it to stand for several days in contact with barium dioxide, dried with fused calcium chloride and distilled, then dried with metallic sodium and redistilled, using a Vigreaux fractionation column. Ostromuislinskii's method of purification by forming the tetrabromide and then removing the bromine by treatment with zinc dust at 0° in absolute alcohol solution was found to be impractical when it was desirable to prepare a liter or more of pure isoprene. The material was colorless; b. p., 33.2–33.8° (742 mm.).

Solvents.—Acetone was freshly distilled over anhydrous potassium carbonate, and the fraction boiling at 56-57° used. Carbon tetrachloride was purified by treatment with saturated chlorine water for several days in diffused sunlight. It was then washed thoroughly with distilled water, dried over fused calcium chloride and distilled.

Experimental Part

When crude rubber, vulcanized rubber or even vulcanite is placed in selenium oxychloride a vigorous reaction sets in and the rubber is dissolved with evolution of heat. The solution becomes reddish brown in color and contains selenium monochloride and selenium, in addition to the decomposition products of the rubber. In order to study this reaction, it became evident at once that the reaction would have to be more carefully controlled and further that the results would be the easier to interpret, the purer the samples of rubber used. The reactions of selenium oxychloride on the purified rubber hydrocarbon in solution in carbon tetrachloride, were carried out in all cases as follows.

To a known quantity of a 5% solution by weight of pure rubber in dry carbon tetrachloride, cooled to 0° , was added slowly, with vigorous stirring, an excess of a 5% solution of selenium oxychloride in dry carbon tetrachloride, also cooled to 0° . The selenium oxychloride was added in slight

- ⁵ Mathews and Strange, Brit. pat., 24,790, 1912.
- 6 Harries, Ann., 383, 157 (1911).
- ⁷ Harries and Gottlob, Ann., 383, 228 (1911).
- 8 Ostromuislinskii, J. Russ. Phys. Chem. Soc., 47, 1983 (1916).

excess as otherwise the solution could not be filtered because the excess of rubber clogs the filter. A yellowish-white, amorphous substance immediately settled. The solution was filtered quickly through a Büchner funnel, the precipitated material transferred to a beaker containing cold carbon tetrachloride and agitated in order to free the material from the slight excess of selenium oxychloride. This operation was repeated several times using fresh portions of cold, dry carbon tetrachloride. The precipitated material was finally brought onto the filter paper and the carbon tetrachloride replaced by ethyl ether. The ether was quickly evaporated, the dry, amorphous powder transferred to a glass-stoppered weighing bottle and this container kept at 0°. Due to its instability at ordinary room temperatures and the consequent evolution of hydrogen chloride, the material had to be handled in this way. This instability also prevented further purification of the material by any of the usual methods.

Table I shows the comparative results based on the averages of all of the complete analyses of the various reaction products of selenium oxychloride with the natural rubbers and the synthetic isoprene rubber

Table I

Average Analyses⁹ of the Products of the Reaction between Rubber and Selenium Oxychloride

	SeOCl ₂ reaction products with	C %	н %	Se %	C1 %	(Diff.) %	Ratio C: H
	"Isoprene Rubber"	23.72	4.67	22.57	23.79	25.25	10:23.3
	Pale Crepe	23.75	4.37	22.81	24.23	24.84	10:22.3
	Smoked Sheet	21.60	4.66	27.04	24.69	22.01	10:26.0
	Para	23.85	4.42	26.74	26.03	18.96	10:22.1
	Caucho Ball	24.49	4.37	26.09	25.35	19.70	10:21.1

Discussion

Attention is called to several points brought out in this table. (1) It will be noted that the average content of carbon in the various reaction products of either synthetic rubber from isoprene, or the natural rubbers, varies less than 1%, except in the case of the product from Smoked Sheet, which is about 2% lower. (2) The average contents of hydrogen in the various reaction products vary less than 0.4 of 1%. (3) The average content of selenium in the synthetic isoprene-rubber product is practically the same as in the plantation Pale Crepe product. The amount of selenium in reaction products of the other 3 natural rubbers, varies only within 1%, but all are 4 to 5% higher than in the case of the Pale Crepe or the synthetic isoprene rubber. It will be noted, however, that the products from all 3 of the natural rubbers in which the latex was coagulated by smoke have a selenium content of 26 to 27%. The Smoked Sheet comes from

⁹ The "average analyses" are the means of the results of 10 to 12 determinations on different samples of the same material handled under as nearly the same conditions as possible. The average analysis for each constituent is accurate to at least 1%.

exactly the same source as the Pale Crepe (cultivated *Hevea brasiliensis*), but the latex of Pale Crepe is coagulated by acetic acid, while the latex of Smoked Sheet is only partially coagulated by acetic acid and is then smoked to complete the process. Possibly this difference in the selenium content of the 2 reaction products can be attributed to the method of coagulation. (4) The average content of chlorine in the various reaction products from either the synthetic or the natural rubber varies about 2.2%. (5) The ratio of carbon to hydrogen has changed from C₁₀H₁₆ in the pure rubber, up to C₁₀H₂₆ in the reaction products. (6) Parallel with the chemical changes in the various kinds of rubber upon treatment with selenium oxychloride, there is a great change in their physical properties. The products are all amorphous powders, having lost their elasticity and swelling power, and are insoluble in the ordinary rubber solvents, such as benzene, carbon tetrachloride, chloroform and ether. (7) The two most important conclusions that can be drawn from the comparative data on these reaction products are: (a) the pure rubber hydrocarbon from natural, *Hevea* rubbers, shows a slightly different behavior in its reaction with selenium oxychloride, depending upon the source of the rubber and its method of coagulation; (b) judging by the behavior towards selenium oxychloride, there is no difference in empirical composition between the pure rubber from a typical natural rubber, such as Pale Crepe, and a synthetic rubber, made by the polymerization of isoprene by metallic sodium. This statement is in contradiction to the recent article of Kirchof. 10 Kirchof has compared the ultimate analyses that have been made on the rubber hydrocarbon from different sources and also the analyses of the various derivatives that have been reported. He concluded that synthetic rubber is a true polymer of the corresponding hydrocarbon, C₅H₈, but that the hydrocarbon of Para rubber has the empirical composition C₁₀H₁₇ and cannot be formed from the hydrocarbon C5H8 through polymerization, as Harries supposed. According to Kirchof, neither the empirical composition nor the structure of synthetic rubber is identical with that of Para rubber.

The present work tends to support the conclusion that Harries reached after a study of the hydrolysis products of the ozonides of various kinds of natural and synthetic rubbers, namely, that there is no essential difference in constitution between natural rubber and the polymerized isoprene.

The author wishes to express his appreciation to Professor Victor Lenher, at whose suggestion and under whose direction this work was carried out; also to Professor Homer Adkins for helpful suggestions.

Summary

1. The reactions between selenium oxychloride and the natural, *Hevea* rubbers, Pale Crepe, Smoked Sheet, Para and Caucho Ball, have been studied.

¹⁰ Kirchof, Kolloidchem. Beihefte, 16, 47 (1922).

- 2. The reaction between selenium oxychloride and a synthetic rubber made by polymerizing isoprene has been studied.
- 3. It has been found that when the various rubbers are treated with selenium oxychloride their physical properties are changed. The products are all amorphous powders, having lost their elasticity and swelling power, and are insoluble in the ordinary solvents for rubber.
- 4. It has been shown that the pure rubber hydrocarbon from natural, *Hevea* rubbers, shows a slightly different behavior in its reaction with selenium oxychloride, depending upon the source of the rubber and its method of coagulation.
- 5. It has been shown definitely that, judging by their respective behaviors towards selenium oxychloride, there is no difference in empirical composition between the pure rubber hydrocarbon from the Hevea tree and the synthetic rubber made by polymerizing isoprene with metallic sodium.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF THE J. B. WILLIAMS COMPANY]

DIPROPARGYL METHYLENE ETHER

By Herbert H. Guest Received April 21, 1923

The statement has been made by Delange¹ that "as a rule, acetylenic linkages produce unpleasant odors.* * * *An exception is methylheptine carboxylate." Apparently, the acetylenic linkage adjacent to an alcoholic group forms another exception of Delange's generalization. For example,³ octin-2-ol-1 has a much pleasanter and more intense odor than octanol. Also,⁴ 2-methylhexin-3-ol-2 has a very pleasant, flower-like odor. Finally, it is well known that propargyl alcohol itself possesses a pleasant odor.

It seemed of interest, therefore, to prepare a number of alcohols having the triple bond in the α position to the hydroxyl group and compare their odors with those of the corresponding saturated alcohols.

The only method so far available for the preparation of these alcohols is that of Moureu and Desmots³ which depends upon the action of trioxymethylene on the sodium derivative of acetylene hydrocarbons. Unfortunately, the latter are not easily obtainable and, moreover, the yield of alcohol is very poor.

This paper describes the attempt to prepare these alcohols by the alkylation of the metallic derivatives of the methylal of propargyl alcohol.

¹ Delange, Perfumery Essent. Oil Record, 13, 352 (1922).

² Moureu and Delange, Bull. soc. chim., [3] 29, 648 (1903).

³ Moureu and Desmots, ibid., [3] 27, 361 (1901).

⁴ Dupont, Compt. rend., 148, 1524 (1909).

This acetal was readily obtained by a method that parallels that of Claisen⁵ for the preparation of propargyl-aldehyde acetals, such as CH: C.CH- $(OCH_3)_2$. The starting point is β -dibromohydrin⁶ which was readily converted into the corresponding acetal. The latter loses 2 molecules of hydrobromic acid on treatment with alcoholic potash to form the acetal of propargyl alcohol: $CH_2Br.CHBr.CH_2OH \longrightarrow (CH_2Br.CHBr.CH_2O)_2-CH_2 \longrightarrow (CH: C.CH_2O)_2CH_2$.

It was hoped that the magnesium-bromide compound, $(MgBrC: C-CH_2O)_2CH_2$, would react with alkyl bromides in a manner analogous to that observed by Grignard⁷ in the preparation of phenylethyl alcohol from phenylmagnesium bromide and glycol chlorohydrin. The action of ethylmagnesium bromide on the acetylenic acetal proceeded normally with a steady evolution of ethane. After some hours or when the ethereal solution was warmed to complete the reaction, a product was formed which was insoluble in ether or benzene. This resinous material has not been identified and is probably the inter-reaction product of 2 or more molecules, in the manner observed by Tschitschibabin and Jelgasin⁸ who found that acetals are acted upon by Grignard reagents to form ethers. When the reaction was stopped before this insoluble substance was produced and alkyl bromide added to the cold mixture, alkylation did not take place.

The silver compound (AgC: C.CH₂O)₂CH₂ was readily obtained but proved to be exceedingly inert. For example, prolonged boiling with excess of butyl bromide failed to give the desired butyl acetal. This result is in harmony with the observation of Reitzenstein⁹ as to the inertness of the silver derivative of the acetal of propargyl aldehyde, AgC: C.CH(OCH₃)₂.

Metallic sodium did not react readily with the acetal of propargyl alcohol and when it was heated for a long time with sodium in toluene suspension a yellow solid was obtained which was not the normal reaction product of acetylenes and sodium.

Experimental Part

Bis(2,3-dibromopropyl)methylene Ether, (CH₂Br.CHBr.CH₂O)₂.CH₂.—Into 342 g. of dibromohydrin dry hydrogen chloride¹⁰ was led until the weight of the mixture had increased 3.5 g.; 135 g. of paraformaldehyde was added and the mixture was allowed to stand at room temperature for 6 days. Ether was added and the excess of paraformaldehyde removed by filtration. The ethereal solution was dried over sodium carbonate. On distillation at 10 mm. pressure, a fraction boiling at 118° to 170° was collected, weighing 76 g., which consisted mostly of unaltered dibromohydrin, and a second fraction boiling at 170–235° which on redistillation gave 195 g. boiling at 220° under 7 mm. pressure. This yield of acetal corresponds to 55%.

⁵ Claisen, Ber., 31, 1022 (1896).

⁶ Kohler, Am. Chem. J., 42, 381 (1909).

⁷ Grignard, Compt. rend., 141, 44 (1905).

⁸ Tschitschibabin and Jelgasin, Ber., 47, 48 (1914).

⁹ Reitzenstein, J. prakt. Chem., [2] 86, 73 (1912).

¹⁰ Fischer and Giebe, Ber., 30, 3053 (1897).

Analysis. Subs., 0.3715: AgBr, 0.6218. Calc. for C₇H₁₂O₂Br₄: Br, 71.43. Found: 71.23.

This acetal was also prepared by the catalytic action of ferric chloride, 11 as follows: 75 g. of dibromohydrin, 25 g. of trioxymethylene and 3.5 g. of sublimed ferric chloride were mixed and heated at $125-150^{\circ}$ for 2 hours. When the product was treated as in the previous case, 18 g. of unaltered dibromohydrin and 42 g. of acetal were obtained, duplicating the percentage yield. Finally, the same results were obtained by the use of dry calcium chloride as catalyst to the extent of 20% of the weight of dibromohydrin taken.

This acetal is a viscous oil, insoluble in alcohol but soluble in ether or benzene.

 $Bis(\alpha\text{-bromo-allyl})$ methylene Ether, $(CH_2: CBrCH_2O)_2CH_2$.—This compound was obtained from the dibrompropyl acetal by the action of a slight excess of finely powdered potassium hydroxide in ether suspension, at a temperature below 25°. The reaction product was treated with water, the oil in ethereal solution dried over calcium chloride and distilled at 10 mm. pressure. On repeated redistillation an oil was obtained, b. p., $135-140^{\circ}$ at 10 mm. pressure, which was soluble in organic solvents.

Analysis. Subs., 0.2773: AgBr, 0.3680. Calc. for $C_7H_{10}O_2Br_2$: Br, 55.9. Found: 56.48.

Dipropargyl Methylene Ether, (CH: $C.CH_2O)_2CH_2$.—To 4 molecular proportions of potassium hydroxide dissolved in 4 times the weight of 95% alcohol and cooled to $25-30^\circ$, one molecular equivalent of the dibromopropyl acetal was gradually added and the mixture kept cold. After $^1/_2$ hour at room temperature, this was heated under a reflux condenser on the steam-bath for 2 to 3 hours. The salt was separated on a filter by suction, the alcoholic filtrate made neutral with acetic acid and then the alcohol removed by distillation under diminished pressure at a low temperature. The residue was poured into water and the oil (400 g.) dissolved in ether, dried over sodium carbonate and distilled at 10 mm. pressure. Fraction 1, b. p. 70–100°, amounted to 98 g.; Fraction 2, b. p. 100–140°, weighed 57 g. and the residue weighed 5 g.

Fraction 1 was redistilled at 10 mm. pressure and the high-boiling portion added to Fraction 2. The united high-boiling fractions were then treated with alcoholic potassium hydroxide as before. On final distillation 56 g. of an oil was obtained which boiled at $75-80^{\circ}$ under 10 mm. pressure and at 162° under 760 mm. pressure; yield, 50%. This oil was free from halogen.

Analyses. Subs., 0.2325: H₂O, 0.1340; CO₂, 0.5730. Calc. for C₇H₈O₂: C, 67.74; H, 6.45. Found: C, 67.22; H, 6.45.

SILVER SALT (AgC: C.CH₂O)₂CH₂.—To a solution of 2 molecular proportions of silver nitrate in a small amount of water and much alcohol, ammonium hydroxide was added by drops until the precipitate that first formed redissolved. One molecular equivalent of acetal dissolved in alcohol was then added, and a white granular precipitate formed at once. This was separated by filtration with suction and washed with alcohol and ether. When dried at 60°, it turned brown; it exploded at 110°. It is insoluble in ammonium hydroxide, alcohol, ether or water.

Analysis. Subs., 0.1825: AgCl, 0.1545. Calc. for C₇H₆O₂Ag₂: Ag, 63.9. Found: 63.71.

This silver salt, while still moist, was added to an ethereal solution of a large excess of butyl bromide. The mixture was heated for 5 to 6 hours under a reflux condenser. As the appearance of the insoluble material did not change, the ether was removed, more butyl bromide added and the whole heated for 5 hours longer. The insoluble material

¹¹ Trillat and Cambier, Bull. soc. chim., [3] 11, 757 (1894).

¹² Compare Adkins and Nissen, This Journal, 44, 2749 (1922).

was removed by filtration and the filtrate distilled. The latter proved to be unaltered butyl bromide.

Action of Grignard Reagent on Acetal.—To a Grignard solution made from 50 g. of ethyl bromide was added gradually at 5–10° an ethereal solution of dipropargyl methylene ether. Ethane was evolved steadily and was collected and tested. After 24 hours outdoors, two layers formed in the liquid. To this mixture was then added 50 g. of butyl bromide, and the whole heated for 3 hours under a reflux condenser; dry toluene was then added and the ether removed. The heating was continued for 1 hour longer. No magnesium bromide separated. The reaction mixture was then treated with dil. sulfuric acid, and the upper layer dried and distilled. After removal of the solvent, no oil was obtained. The residue, which was insoluble in solvents, could not be resolved into any individual product.

This experiment was repeated several times under various conditions, but so far unsuccessfully.

Summary

- 1. Dipropargyl methylene ether was prepared from the acetal of β -dibromohydrin.
- 2. It was found that the silver derivative of dipropargyl methylene ether did not react with alkyl halides under the conditions indicated.
- 3. Dipropargyl methylene ether reacts with ethylmagnesium bromide but the resulting reaction product did not aid in the synthesis of the higher homologs of propargyl alcohol.

GLASTONBURY, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, HARVARD MEDICAL SCHOOL]

OBSERVATIONS ON THE PROPERTIES OF ARSPHENAMINE¹

By Walter G. Christiansen Received April 26, 1923

The Relation of Arsphenamine to Some Methyl Ketones

In connection with an investigation of the ease of solution of arsphenamine in water, samples were precipitated from methyl alcohol solution by acetone instead of ether. Analytical data on material precipitated in this way confirm the conclusion of Fargher and Pyman² that the product contains 1 molecule of acetone in addition to the usual 2 molecules of water.

Calc. for $C_{12}H_{14}O_2N_2Cl_2As_2.2H_1O.(CH_3)_2CO$: As, 28.2; Cl, 13.3. Found: As, 28.1; Cl, 13.1.

Prolonged drying in a vacuum removes the 2 molecules of water but the acetone remains unchanged;² when the material is dried to constant

¹ This is the twelfth of a series of studies on the properties contributing to the toxicity of arsphenamine being made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School; the work is under the general direction of Dr. Reid Hunt.

² Fargher and Pyman, J. Chem. Soc., 117, 372 (1920).

weight at about 98° in a slow stream of dry carbon dioxide the loss is that calculated for 2 molecules of water and the dried product gives a strong qualitative test for acetone.

Calc. for 2 H₂O: H₂O, 6.7. Loss at 98°: 6.1.

Moreover, when arsphenamine containing a molecule of acetone is dissolved in absolute methyl alcohol and reprecipitated with ether, the dried product still gives a very positive test for acetone. Since neither drying or reprecipitation from acetone-free solvents removes the acetone, the latter must be bound very firmly to the arsphenamine molecule and is not retained mechanically. In view of this strong union, one would expect that if a small amount (0.5 cc.) of acetone be added to a methyl alcohol solution of arsphenamine (1 g. in 8 cc. of methyl alcohol) before the latter is poured into ether, the product, after it is washed and dried, would contain acetone; this has been found to be true. In similar experiments using methylethyl, methyl-n-propyl, methyl-n-butyl, and methylisobutyl ketone, instead of acetone, the products always give positive tests for methyl ketone.

From the work described above it is evident that arsphenamine possesses a strong affinity for methyl ketones. The tests for ketones were made by testing with alkali and iodine the first portions of the distillate of a 5% aqueous solution of the arsphenamine.

The Conversion of Arsphenamine Into a Polyarsenide

The reduction of a mixture of 2 different aryl arsonic acids or the digestion of a mixture of 2 symmetrical aryl arseno compounds always results in the formation of 1 unsymmetrical arseno compound. Also, when an arsonic acid is reduced in the presence of an inorganic arsenical, an organic polyarsenide, such as Ar₂As₄, is formed instead of a mixture of ArAs = AsAr and metallic arsenic. It has now been found that an arseno compound in the presence of nascent arsenic changes to a polyarsenide.

A solution of 0.2 g. of arsphenamine in 3.2 cc. of water is treated with 2.4 cc. of 50% hypophosphorous acid, 0.4 cc. of hydrochloric acid (d., 1.19) and 3.2 cc. of an aqueous solution of sodium arsenite (1 g. of NaAsO₂ in 16 cc. of solution). The pale yellow solution, in a stoppered cylinder, is allowed to st and at room temperature in the dark; it becomes orange colored, and then red; turbidity sets in and finally a precipitate forms. When the material stands long enough, the solution becomes colorless and the orange-colored precipitate becomes covered by a black layer of metallic arsenic. Before this stage is reached, the mixture of orange-colored solid and solution is poured into 2 volumes of 1 to 1 cold hydrochloric acid and the solid is washed with acid and dried in a vacuum over sodium hydroxide. From 1.3 g. of arsphenamine, 1.7 g. of a red polyarsenide of arsphenamine is obtained.

Analysis. Calc. for C₁₂H₁₄O₂N₂Cl₂As₄: As, 50.9. Found: 52.5.

When a mixture of 3-amino-4-hydroxyphenyl-arsenious oxide and sodium arsenite in aqueous solution containing hydrochloric acid, is reduced with hypophosphorous acid and the polyarsenide isolated as described above, a red solid is obtained which contained 53.7% of arsenic and dissolves in water to give a red solution.

The rate of polyarsenide formation as determined by the color change and appearance of turbidity varies greatly depending upon the method of preparation of the arsphenamine. The following methods are arranged in the order in which resulting arsphenamine undergoes polyarsenide formation with decreasing speed: (1) reduction of 3-nitro- or 3-amino-4-hydroxyphenylarsonic acid with pure hydrosulfite; (2) reduction of the nitro acid to toxic arsphenamine with commercial hydrosulfite; (3) reduction of the amino acid or the nitro acid to relatively non-toxic arsphenamine with commercial hydrosulfite; (4) reduction of the amino acid with hypophosphorous acid followed by precipitation with hydrochloric acid.

When a sample which gives the polyarsenide reaction quite rapidly is allowed to stand in aqueous solution with a small amount of hydrochloric acid, the viscosity of the solution increases and the rate at which it is converted into a polyarsenide decreases. Also, when a specimen of arsphenamine base which gives a polyarsenide fairly rapidly is converted into the dihydrochloride the latter gives a polyarsenide less rapidly than the original base. It seems that the rate at which this reaction takes place is closely connected with the degree of polymerization³ of the arsphenamine.

The Precipitation of Dilute Aqueous Solutions of Arsphenamine with Hydrochloric Acid

During the investigation of the reduction of 3-nitro-4-hydroxyphenylarsonic acid to arsphenamine base with commercial hydrosulfite, it was
shown that the conditions under which the nitro group is reduced exert a
great influence on the toxicity of the product; and two sets of conditions
were developed, one of which favored the formation of toxic products
whereas the other enabled one to obtain products of low toxicity. In
both procedures the quantities of reagents are identical. Mr. George, of
this Laboratory, has examined the action of precipitants on dilute aqueous
solutions of a number of samples of arsphenamine and finds that the amount
of hydrochloric acid required to precipitate a solution of a specimen prepared under the conditions most favorable to the development of low toxicity is nearly twice as great as that required for the toxic specimen prepared under the other procedure.

Two-tenths cc. of a 2% solution of alkalinized arsphenamine, that is, one containing the disodium salt of arsphenamine, is diluted with 1 cc. of water in a 7 cc. test-tube which is then placed in a water-bath at 37°. Hydrochloric acid (1:1) is added from a small buret until a permanent precipitate is secured. All specimens prepared under the most favorable conditions require 1.95 cc. of acid and those prepared under the least favorable conditions require only 1.12 cc.

When marked changes are made in the preparation of the arsphenamine, such as changes in the acidity of the reduction mixture, the hydrochloric

³ Sherndal, J. Lab. Clin. Med., 7, No. 12 (1922).

acid titration fluctuates greatly from the values given above. Since the amount of hydrochloric acid is constant only when every detail of the preparation of the arsphenamine is exactly duplicated each time, this titration is a rapid way to detect variations in the routine preparation of this material, and specimens giving a low precipitation value should be carefully examined toxicologically.

The precipitation of arsphenamine from aqueous solutions with hydrochloric acid is a salting-out process and involves the coagulation of the finely divided arsphenamine particles in the original solution. Since the less toxic specimens require more acid than the relatively toxic ones, the arsphenamine is in a more finely divided state in the less toxic solutions. This difference in the state of division may account for some of the unfavorable results encountered in the more toxic material.

The Importance of the Quantity of Hydrochloric Acid Used in Converting Arsphenamine Base into the Hydrochloride

In the common method of converting arsphenamine base into the hydrochloride the base is dissolved in methyl alcoholic hydrochloric acid and this solution is mixed with a large amount of ether to precipitate the arsphenamine. The quantity of hydrochloric acid used in this process has considerable bearing on the physical properties of the resulting arsphenamine. If only 1 molecule of acid per molecule of base is used, the alcohol solution is dark colored; in extreme cases, as when the nitro acid has been reduced improperly, the color may be reddish-brown. As more acid is added, the color changes gradually to a clear yellow. The dark colored solution of the monohydrochloride, poured into ether, gives a gummy and dark colored precipitate; part of the solid remains suspended in the ether and cannot be filtered out easily. When more methyl alcoholic hydrochloric acid is added to the ether suspension, the precipitate coagulates and settles at once. When a solution of the base in methyl alcohol containing 2 or a fraction more molecules of hydrochloric acid is poured into ether, the yellow precipitate coagulates at once and the supernatant liquor is perfectly clear. In order to secure the desired yellow color and to obtain a precipitate that can be manipulated easily it is advisable to use a slight excess of acid over that necessary to form the dihydrochloride.

The amount of acid used in preparing the hydrochloride has very little bearing upon the toxicity and sulfur content of the product. It has been noted, however, that material made with less than 2 molecules of acid produces death more quickly than material prepared with an excess of acid, when administered in fatal doses to rats.

I wish to thank Dr. Reid Hunt for his interest in this work, and Mr. Arthur Norton for preparing the higher methyl ketones.

Summary

Arsphenamine forms additive compounds with methyl ketones in which the ketone is bound very firmly. Neither drying at room temperature or at 98°, nor reprecipitation from ketone-free methyl alcohol with ether removes the ketone. When an aqueous solution of arsphenamine and sodium arsenite is treated with hydrochloric and hypophosphorous acids. the yellow color gradually changes to red and a polyarsenide of arsphenamine is formed. The rate at which this reaction takes place depends upon the method used in preparing the arsphenamine and seems to be related to the physical properties of the latter. The quantity of 1 to 1 hydrochloric acid necessary to precipitate a dil. aqueous solution of arsphenamine is constant when one method of preparation is strictly followed, but slight variations in certain steps in the synthesis cause fluctuations in the amount of acid required. Therefore, this titration has been found useful in determining the closeness with which the routine method of preparation has been followed. The physical properties of arsphenamine are affected materially by the amount of hydrochloric acid used in converting the base into the hydrochloride; it is advantageous to use a slight excess over the two molecules needed to secure the dihydrochloride.

Boston 17, Massachusetts

[Contribution from the Department of Chemical Research, Parke, Davis and Company, No. 18]

5,5-DIARYLBARBITURIC ACIDS

By Arthur W. Dox and Adrian Thomas Received April 30, 1923

Considering the great importance of veronal (diethylbarbituric acid) and luminal (phenylethylbarbituric acid) as therapeutic agents, and the large number of homologs that have been prepared by substituting other alkyl groups, it is surprising that no attempts to prepare 5,5-diarylbarbituric acids are on record. Luminal, in which one of the ethyl groups of veronal has been replaced by phenyl, is said to be 2.5 times as powerful in its physiological action as veronal, and is widely used in the treatment of epilepsy. The introduction of a second phenyl group might be expected to increase the physiological activity still further, provided the resulting derivatives possessed certain essential physical properties. The isomeric 1,3-diphenylbarbituric acid has been prepared by Whiteley¹ from malonyl chloride and carbanilide. No statement is made regarding its physiological properties, but from analogy with other N-substituted barbituric acids, we should hardly expect this substance to be of medicinal value.

The substitution of one or more aryl groups on the 5-carbon atom of Whiteley, J. Chem. Soc., 91, 1330 (1907).

barbituric acid is much more difficult than the substitution of alkyl groups. Some of the more reactive alkyl halides, such as allyl bromide² and benzyl chloride,³ react directly with barbituric acid or a mono-alkyl substituted barbituric acid. Other alkyls, as ethyl and its homologs, must be introduced in a previous step of the synthesis, as in the alkylation of an alkyl malonate before condensation with urea. An aryl halide, on the other hand, cannot be made to react with an alkyl malonate. The aryl group, in luminal, for example, is added in a still earlier step of the synthesis. The addition of a second aryl would naturally be attended by further complications.

The most satisfactory method for the preparation of 5,5-dialkylbarbituric acids is the condensation of an ester of the corresponding dialkylmalonic acid with urea.⁴ An ester of a diarylmalonic acid might, therefore, be expected to condense with urea in the same manner. The simplest derivative of this type, methyl diphenylmalonate, was prepared by Staudinger, Göhring and Schöller,⁵ from the acid chloride obtained by treatment of diphenylketene with oxalyl chloride. Obviously, this method is too costly to be of practical importance.

Several alkyl diarylmalonates have been prepared by Guyot and Esteva⁶ by condensing aromatic hydrocarbons with alkyl oxomalonates in the presence of concd. sulfuric acid. In this reaction water is split out and 2 products are formed, an alkyl aryltartronate and an alkyl diarylmalonate, the amount of the latter depending upon the temperature and time of reaction. Guyot and Esteva describe the methyl and ethyl esters of ditolyl- and di-o-xylylmalonic acids. The lower homolog, diphenylmalonic ester, they evidently did not succeed in obtaining, although the methyl and ethyl esters of phenyltartronic acid are mentioned.

By the method of Guyot and Esteva the writers succeeded in preparing ethyl diphenylmalonate, but all attempts to condense this with urea were unsuccessful. The substance appears to lack the stability of the dialkylmalonic esters, and when treated with sodium ethylate and urea it readily loses a carboxyl group. No evidence of the formation of a diphenylbarbituric acid was obtained; the only products identified were diphenylacetamide and diphenylacetic acid. Likewise, ethyl di-ptolylmalonate, prepared by the same method, gave only the corresponding acetamide and the substituted acid. However, the diphenylmalonic esters are apparently more stable when an hydroxyl is present on the benzene nucleus. Thus, from ethyl di-(p-hydroxyphenyl)malonate we obtained by the usual method, di-(p-hydroxyphenyl)barbituric acid.

² U. S. pat., 1,042,265, 1912.

³ Dox and Yoder, This Journal, 44, 1144 (1922).

⁴ Fischer and Dilthey, Ann., 335, 334 (1904).

⁵ Staudinger, Göhring and Schöller, Ber., 47, 43 (1914).

Guyot and Esteva, Compt. rend., 148, 564 (1909).

This is the first diarylbarbituric acid containing 2 aromatic hydrocarbon radicals attached directly to the 5-carbon atom. It is isomeric with 5,5-diphenoxybarbituric acid in which the aryl groups are joined to the pyrimidine nucleus through oxygen.

Experimental Part

Ethyl Diphenylmalonate.—Ethyl oxomalonate was prepared by oxidation of ethyl malonate with nitrous anhydride. Thirty g. of this product was dissolved in 90 g. of anhydrous benzene, and 60 g. of concd. sulfuric acid added. The sulfuric acid layer became purplish-blue and some heat was developed. The flask was then immersed in an oil-bath at 70° and the mixture mechanically stirred for 7 hours, after which it was poured on cracked ice and the sulfuric acid removed by agitation with several lots of water. The excess of benzene was removed by distillation, and the residue distilled in a vacuum. The main product consisted of 17.5 g. of a thick, yellow oil; b. p., 180–200° (9 mm.). After several days a few crystals appeared in this oil and when it was then stirred with a glass rod the entire mass solidified. It was purified by drying on a porous plate and recrystallizing from alcohol in which it is readily soluble. The product consisted of small white prisms; m. p., 58–59°.

Analyses. Subs., 0.1961: H_2O , 0.1110; CO_2 , 0.5281. Calc. for $C_{19}H_{20}O_4$: H, 6.41; C, 73.08. Found: H, 6.29; C, 73.45.

From the mother liquor a small amount of a product melting at $27-28^{\circ}$ was obtained. This corresponds to Guyot and Esteva's ethyl phenyltartronate.

Condensation of Ethyl Diphenylmalonate with Urea.—In our first experiment Fischer and Dilthey's veronal method was employed. A mixture consisting of 5.0 g. of ethyl diphenylmalonate, 1.5 g. of urea, and 1.5 g. of sodium dissolved in 25 cc. of absolute alcohol was heated in an autoclave at 106–108° for 7 hours. The product was neutralized with hydrochloric acid, filtered, diluted with water and evaporated; 2.5 g. of colorless crystals was thus obtained. Treatment with cold dil. alkali dissolved 1.0 g. and this was again recovered by acidifying the solution. The substance consisted of white needles; m. p., 145°. A qualitative test for nitrogen was negative. In making this test the characteristic orange odor of diphenylmethane was noted. This substance would result from simple loss of carbon dioxide from diphenylacetic acid. The neutralization constant of the acid was 222; calc. for C₁₄H₁₂O₂, 212. The substance was undoubtedly diphenylacetic acid.

The portion of the reaction product insoluble in dil. alkali was recrystallized from alcohol; m. p., $169-170^{\circ}$. The nitrogen content was 6.80%; calc. for $C_{14}H_{13}NO$, 6.63%. This identified the substance as diphenylacetamide.

Ethyl diphenylmalonate, in its instability toward sodium ethylate, is in striking contrast to the diethylmalonate which is saponified only with difficulty. In their preliminary paper, Guyot and Esteva⁸ state that the free diarylmalonic acids could not be obtained, since treatment of the esters with alcoholic potash split out carbon dioxide and gave the corresponding diarylacetic acids. We attempted, therefore, the condensation with urea under less drastic treatment, using a lower temperature and 1 mole of sodium instead of 3. Nevertheless, the same products resulted, and in about the same proportions. No barbituric acid derivative could be isolated.

Condensation of Ethyl Di-p-tolylmalonate with Urea.—Ethyl di-p-tolylmalonate was prepared in a similar manner from ethyl oxomalonate, toluene and sulfuric acid; m. p., 91-92°; Guyot and Esteva report a melting point of 93.5°. When heated with

⁷ Curtiss, Am. Chem. J., 35, 478 (1906).

⁸ Guyot and Esteva, Bull. soc. chim., [4] 3, 803 (1908).

urea in the presence of sodium ethylate it gave two products which were readily separated by treatment with cold dil. alkali. The acid product contained no nitrogen and melted at 140–141°; the recorded melting point of di-p-tolylacetic acid is 144°.

Di-p-tolylacetamide.—The alkali-insoluble product from the condensation described above was recrystallized from dil. alcohol and obtained in white needles melting at 190°. The substance is almost insoluble in water, but is readily soluble in alcohol.

Analyses. Subs., 0.2, 0.2: cc. of 0.1 N NH₃, 8.2, 8.2. Calc. for $C_{16}H_{17}NO$: N, 5.81. Found: 5.74, 5.74.

Again no barbituric acid derivative was obtained.

Ethyl Di(p-hydroxyphenyl)malonate.—Ten g. of phenol was dissolved in 10 g. of ethyl oxomalonate. A considerable lowering of temperature resulted. Dry hydrogen chloride was passed in, and the solution was finally immersed in a freezing mixture and saturated with the gas. A viscous oil was obtained, which crystallized after several days at 0°. The crystals were dried on a porous plate and recrystallized from a large volume of hot water. Flat lustrous needles were obtained; m. p., 133–134°. The substance was difficultly soluble in water, readily soluble in alcohol and in dil. aqueous alkali. It gave a blue color with ferric chloride.

Analyses. Subs., 0.2022, 0.2016: H_2O , 0.1026, 0.1024; CO_2 , 0.4828, 0.4782. Calc. for $C_{21}H_{24}O_6$: H, 5.86; C, 66.24. Found: H, 5.69, 5.71; C, 65.12, 64.88.

5,5-Di(p-hydroxyphenyl)barbituric Acid.—The ester described above was autoclaved in the usual manner with urea and sodium ethylate. The reaction mixture was acidified, diluted with water and evaporated. The product separated first as an oil which soon solidified. Recrystallization from hot water gave small slender needles; m. p., 288–290°. The substance is moderately soluble in hot water, readily soluble in dil. alkali and in alcohol. From 7.5 g. of the ester 3.0 g. of the barbituric acid was obtained. This substance also gives the ferric chloride reaction.

Analyses. Subs., 0.2, 0.2: 12.4, 12.5, cc. of 0.1 N NH₃. Calc. for $C_{16}H_{12}N_2O_6$: N, 8.97. Found: 8.68, 8.75.

Ethyl Diphenoxymalonate.—Ten g. of sodium was dissolved in 200 cc. of absolute alcohol, the solution cooled in ice water and 40 g. of phenol added. To the cold sodium phenylate 75 g. of ethyl dibromomalonate was gradually added with stirring. The mixture was refluxed for 1 hour and then found to be neutral to litmus. The alcohol was distilled in a vacuum and the remaining oil washed with water and dried with calcium chloride. Distillation under diminished pressure gave 45 g. of an oil; b. p., 195–204° (6 mm.).

Analyses. Subs., 0.2518, 0.2502: H_2O , 0.1254, 0.1298; CO_2 , 0.5996, 0.5962. Calc. for $C_{21}H_{24}O_6$; H, 5.86; C, 66.24. Found: H, 5.58, 5.81; C, 64.94, 64.98.

5,5-Diphenoxybarbituric Acid.—The ester described above was heated in an autoclave with urea and sodium ethylate. The barbituric acid was isolated by the usual procedure and recrystallized from a mixture of benzene and alcohol. From 11.5 g. of the ester we obtained 6.5 g. of the barbituric acid in very fine white needles melting at 192°. The substance is nearly insoluble in water, difficultly soluble in benzene and readily soluble in alcohol; it is intensely bitter. It is isomeric with the di(p-hydroxyphenyl)-barbituric acid described above.

Analyses. Subs., 0.2, 0.2: ec. of 0.1 N NH₃, 12.6, 12.5. Calc. for C₁₆H₁₂N₂O₅: N, 8.97. Found: 8.82, 8.75.

Ethyl Di-(4-hydroxy-3-methylphenyl)-malonate.—A solution of 14 g. of o-cresol in 12 g. of ethyl oxomalonate was saturated at 0° with dry hydrogen chloride. After 4

⁹ Fritsch and Feldmann, Ann., 306, 81 (1899).

days the mass had solidified. The crystals were dried by suction and washed with water. Two recrystallizations from dil. alcohol gave 16 g. of short white prisms; m. p., 107–108°. From alcoholic solution water precipitated the substance as an oil which gradually solidified. A blue color is obtained with ferric chloride.

Analyses. Subs., 0.2504, 0.2514: H₂O, 0.1406, 0.1394; CO₂, 0.6158, 0.6220. Calc. for C₂₃H₂₈O₆: H, 6.49; C, 67.77. Found: H, 6.29, 6.22; C, 67.07, 67.47.

5,5-Di-(4-hydroxy-3-methylphenyl)-barbituric Acid.—Five g. of the ester obtained as described above, 2 g. of urea and 1.4 g. sodium dissolved in 25 cc. of absolute alcohol were heated in an autoclave for 7 hours at 107–109°. The usual treatment then gave an oil with a strong odor of cresol. The product was obtained in crystalline form by dissolving the oil in a small amount of absolute alcohol and adding petroleum ether. Recrystallization from dil. alcohol gave 1 g. of white prisms melting at 217–219°. The substance is insoluble in water, readily soluble in alcohol, odorless and tasteless, and in dil. alcoholic solution gives a blue color with ferric chloride.

Physiological Tests

The two isomers, $\operatorname{di}(p\text{-hydroxyphenyl})$ barbituric acid and diphenoxy-barbituric acid, were tested physiologically. A 3% solution, prepared by dissolving the substance in a minimum amount of dil. alkali, was injected intraperitoneally into white mice in the proportion of 0.02 cc. per g. of body weight. This corresponds to twice the effective dose of veronal. The mice were kept under observation for several hours, but no symptoms of somnolence were observed or even muscular incoördination. Veronal, when administered in the same way in doses 1/2 as great, produces a profound state of coma within 15 minutes. We must conclude, therefore, that the two barbituric acid derivatives described above are physiologically inert, at least in moderate doses.

An examination of the structure of the synthetic hypnotics commonly used shows that practically all are aliphatic derivatives. Where an aromatic grouping is present, as in luminal and in phenylethyl-hydantoin, the aromatic group comprises a relatively small part of the molecule. On the other hand, aromatic derivatives for which hypnotic properties might be predicted, on the basis of their distribution coefficient and molecular stability, are generally inert. Acetophenone perhaps comes the nearest to being an aromatic hypnotic, but a further increase in the aromatic groupings, as in benzophenone and diphenylcarbinol, causes the hypnotic action to disappear. It is of interest to note that the 2 barbituric acids under discussion consist essentially of 2 benzene rings and 1 pyrimidine ring, that is, they are predominatingly aromatic. The hydantoins furnish a parallel case: phenylethyl-hydantoin, mainly aliphatic, is an hypnotic while diphenyl-hydantoin, mainly aromatic, is not. Further evidence is, of course, required to establish this point, but from the data at hand it would appear that a search for hypnotics among derivatives that are essentially aromatic is not very promising.

Summary

Ethyl diphenylmalonate and ethyl di-(p-tolyl)malonate when subjected to the usual treatment with urea and sodium ethylate for condensation into a barbituric acid undergo decomposition with loss of a carboxyl group. When, however, the phenyl groups carry an hydroxyl group, as in ethyl di(p-hydroxyphenyl)malonate and ethyl di-(3-methyl-4-hydroxyphenyl)malonate the condensation to a 5,5-diarylbarbituric acid is readily effected. Neither 5,5-di(p-hydroxyphenyl)barbituric acid nor its isomer, 5,5-diphenoxybarbituric acid, shows noticeable hypnotic properties. Attention is called to the fact that these derivatives differ from the great majority of synthetic hypnotics in that they are predominantly aromatic.

DETROIT, MICHIGAN

[Contribution from the Massachusetts Institute of Technology, Laboratory of Organic Chemistry]

THE UREA DEARRANGEMENT. II

By Tenney L. Davis and Kenneth C. Blanchard Received May 8, 1923

Just as urea dearranges into ammonia and isocyanic acid, so substituted ureas, thio-urea and guanidine, and their substitution products dearrange in similar fashion. When urea is heated with aniline, the isocyanic acid which is formed combines with the aniline to form phenylurea. This substance dearranges in two modes to form on the one hand aniline and isocyanic acid, on the other phenylisocyanate and ammonia; the phenylisocyanate and aniline combine to produce sym-diphenylurea which can dearrange in only one fashion to regenerate the substances from which it was produced. In the first paper¹ of this series, experiments were described which elucidate the mechanism of these reactions. By heating the dry materials together at about 160° we were able to prepare a number of derivatives of various aromatic primary amines.

In continuing the study we now find that the reactions take place in boiling aqueous solution. If urea and aniline hydrochloride are boiled together in water solution under a reflux condenser, phenylurea is formed and remains in solution in the hot liquid. After the clear solution has boiled for some time, diphenylurea begins to precipitate. Diphenylurea may be filtered from the hot liquid, and monophenylurea may be obtained by cooling the filtrate. By suitable modifications of the process, by repeating the boiling and filtration, it is possible to obtain either or both of the products in excellent yield. We find also that phenylurea refluxed in water solution yields sym-diphenylurea just as it does when heated at 160° in the dry state. When its aqueous solution is distilled, aniline passes over.

¹ Davis and Underwood, This Journal, 44, 2595 (1922).

In the aliphatic series, we have prepared sym-dimethylurea, diethylurea, di-n-butylurea, di-n-amyl-, di-iso-amyl-, benzyl- and dibenzylurea, by heating the amine hydrochloride with urea at 160–170° or by boiling the amine or its hydrochloride with urea in aqueous solution under a reflux condenser. When the amine hydrochloride was heated with urea, the amount of ammonium chloride which was produced indicated that the reaction had proceeded nearly to completion, but the aliphatic ureas are troublesome to manipulate and the yields of actual product, while considerable, were not as good as in the aromatic series.

When a solution of urea was refluxed with methylaniline hydrochloride and with ethylaniline hydrochloride, the corresponding unsymmetrical disubstituted ureas were produced. The yields were poor, but there was no evidence of tetrasubstituted urea, a fact which accords with our belief that the unsymmetrical disubstituted ureas dearrange in only one fashion: $RR'N-CO-NH_2 \longrightarrow RR'NH + HNCO$. The poor yields may perhaps have been due to the hydrolytic action of the amine hydrochloride solution on the isocyanic acid leading to the formation of ammonia and carbon dioxide, a belief which is supported by the fact that an increasing amount of the free base precipitated out as the boiling was continued.

Striking evidence of the dearrangement of substituted ureas was found in the interaction of aniline with sym-diethylurea. Diethylurea dearranges in only one fashion: C_2H_5NH —CO— NHC_2H_5 \rightleftharpoons C_2H_5NCO + $C_2H_5NH_2$. When it is heated with aniline, ethyl amine escapes and the ethyl isocyanate combines with the aniline to form sym-ethylphenylurea. This substance now dearranges in two modes: $C_2H_5NH_2$ + C_6H_5NCO \rightleftharpoons C_2H_5 —NH—CO— NHC_6H_5 \rightleftharpoons $C_6H_5NH_2$ + C_2H_5NCO . When it is heated alone, the more volatile substances escape and the aniline and phenylisocyanate combine to form sym-diphenylurea. The same product is formed more quickly if sym-diethylurea or sym-ethylphenylurea is heated with an excess of aniline.

Discussion of Experiments

Phenylated Urea.—A solution of 190 g. of urea and 390 g. of aniline hydrochloride in a liter of water was boiled under a reflux condenser. At the end of an hour crystals of sym-diphenylurea suddenly separated from the liquid. The boiling was continued until the mixture bumped, the hot liquid was filtered at the pump, the diphenylurea was washed on the filter with hot water, and the filtrate on cooling deposited crystals of phenylurea. This material was separated, and the filtrate was again boiled under a reflux condenser until it bumped, again filtered hot, again cold, and again refluxed. After four such boilings the final filtrate was evaporated to half volume for another small crop of each of the products. The diphenylurea accumulated from the hot filtrations was practically pure, m. p., 235°, and weighed 80.3 g., a yield of 25.5%. It was obtained in splendid, colorless needles by recrystallization from alcohol, 1 liter of solvent for every 25 g. of the material. The phenylurea from the cold filtrates amounted to 218.5 g.; yield, 53.5%. It was freed from the small amount of diphenylurea which it contained

by dissolving it in hot water, filtering, allowing to cool slightly until a flocculent precipitate of diphenylurea had appeared, and again filtering quickly without warming, and obtained as colorless needles or flakes; m. p., 147°.

A solution of 60 g. of urea and 300 g. of aniline hydrochloride in a liter of water was boiled under a reflux condenser for about 2 hours until the mixture bumped. The precipitated diphenylurea was filtered from the hot liquid and rinsed with a little hot water, the filtrate was returned at once to the flask and refluxed again until bumping recommenced, again filtered, etc. After four boilings the accumulated diphenylurea amounted to 192 g.; yield, 90%. The melting point indicated that the product was practically pure, but its appearance was improved greatly by recrystallization from alcohol with a little animal charcoal.

One experiment in which aniline itself was refluxed with a water solution of urea gave a good yield of the two products. One in which aniline and urea were refluxed in alcohol solution and the alcohol and excess aniline were removed by distillation with steam, gave a very poor yield, the reaction evidently not taking place to any great extent in alcohol and the products being probably formed during the distillation.

The reaction does not take place at ordinary temperatures. A solution of 30 g. of urea and 64.5 g. of aniline hydrochloride in 100 cc. of water was allowed to stand for 4 months in a stoppered flask. It was then extracted thoroughly with ether. The extract on evaporation yielded a residue too small in amount for a melting-point determination.

When a clear solution of 5 g. of phenylurea in 50 cc. of distilled water was boiled under a reflux condenser, it soon became turbid from the separation of small crystals. The crystals filtered from the hot liquid after 3 hours' boiling weighed 0.9 g. and were found to be pure diphenylurea; m. p., 235°. Further evidence of the dearrangement of phenylurea is found in the fact that its aqueous solution yields aniline on distillation. Six g. of phenylurea was dissolved in 250 cc. of water and the solution was distilled, more water being added, until a liter of distillate had been collected. An excess of bromine water was added to the distillate, and the mixture was extracted with chloroform. The chloroform on evaporation yielded 3.6 grams of residue which, recrystallized from chloroform, gave needles, m. p. 121°, identified as tribromo-aniline by mixed melting point with a known sample.

Methylated Urea.—A mixture of 13.5 g. of methylamine hydrochloride and 6 g. of urea was heated for 1 hour at 160-170°. The mass was extracted with boiling absolute alcohol and filtered for the removal of undissolved ammonium chloride. The alcohol solution was evaporated in a vacuum nearly to dryness. More ammonium chloride separated. This was removed by filtration and rinsed with ice cold absolute alcohol. Crystallization of the liquors yielded 6.9 g. of sym-dimethylurea, as colorless flakes, m. p., 99.5-100°; yield, 78.4%.

Ethylated Urea.—A mixture of 30 g. of ethylamine hydrochloride and 11.1 g. of urea was heated for 2 hours at 160-170°. Extraction of the product with absolute ether left a residue of 18.1 g. of ammonium chloride (90% yield) which indicated that the reaction had proceeded nearly to completion. The ether on evaporation yielded a pasty mass which, worked up from alcohol, gave 9.2 g. of sym-diethylurea as colorless needles; m. p., 112°; yield, 43%. The residue from the crystallization was a viscous, heavy, colorless sirup from which nothing further could be obtained.

Replacement of Ethyl by Phenyl.—A mixture of 4 g. of sym-diethylurea and 3.1 g. of aniline was heated at 160-170°. The material melted completely, ethylamine and ammonia were given off immediately, and after about 25 minutes needle crystals began to separate from the hot liquid. After an hour, the mixture was cooled and filtered with suction. The crystals, washed with alcohol and recrystallized from the same solvent, yielded sym-diphenylurea; m. p., 235°. The filtrate was kept in a vacuum until the

aniline had evaporated. The residue, recrystallized from a mixture of water and alcohol, yielded 0.2 g. of fine white needles, m. p., 98–99°, identified as sym-ethylphenylurea by a mixed melting point with a sample prepared by the interaction of phenylisocyanate with ethylamine in toluene solution.

Two g. of sym-ethylphenylurea was heated for $1^1/2$ hours at $160-170^\circ$. Ethylamine was evolved. The residue taken up in hot alcohol yielded on cooling 1.3 g. of sym-phenylurea as needle crystals; yield, 80%.

Butylated Urea.—A solution of 8 g. of *n*-butylamine and 3.3 g. of urea in 50 cc. of water was refluxed for $2^{1}/_{2}$ hours. The solution was evaporated to dryness, and the residue, dried in the steam oven and recrystallized from benzene, yielded 6.5 g. of symdi-*n*-butylurea, as white flakes, sparingly soluble in water; m. p., 70.5– 71.0° ; yield, 70%.

Analysis. Calc. for C9H20ON2: N, 16.28. Found: 16.15.

An experiment with the hydrochloride gave a similar result; 21 g. of *n*-butylamine was converted to the hydrochloride by treatment with hydrochloric acid and evaporated to dryness. When the resulting material was refluxed for 3 hours with 8.3 g. of urea in 150 cc. of water, the solution evaporated to dryness, and the residue extracted with ether for the separation of the product from ammonium chloride, the product recrystallized from benzene amounted to 17.3 g. of di-*n*-butylurea; yield, 71.7%.

Sym-di-n-butylurea heated with aniline at 160–170° yielded sym-diphenylurea, as expected. A small quantity of another substance was isolated as white flakes, m. p., 65°, which was possibly sym-n-butylphenylurea, but not enough was obtained for analysis.

We have not been able to prepare *unsym*-di-n-butylurea by boiling the secondary amine or its hydrochloride with a water solution of urea under a reflux condenser or by heating the hydrochloride with urea at 160-170°.

n-Amyl and iso-Amyl Urea.—Three and three-tenths g. of n-amylamine, b. p., 99-108°, prepared by the reduction of n-butyl cyanide, was converted to the hydrochloride, and the resulting dry product was heated with 1.1 g. of urea for 2 hours at 160-170°. The product was broken up under hot alcohol and filtered. Water was added to the filtrate until a turbidity began to appear. The crystals collected from the cold liquid amounted to 0.8 g. of crude product; m. p., 84-85°. By recrystallization from hot water, pure sym-di-n-amylurea was obtained as white flakes; m. p., 92.8°.

Analysis. Calc. for C₁₁H₂₄ON₂: N, 13.99. Found: 13.93.

A mixture of 5 g. of *iso*-amylamine hydrochloride and 1.2 g. of urea was heated for 3 hours at 160–170°. When the melt was treated with water, a light yellow oil separated. This was extracted with ether, and the ether solution, dried with fused sodium sulfate and allowed to evaporate, deposited an oil. When this oil was distilled in a vacuum, the first portion had an odor of isonitrile and did not crystallize, while the later portion crystallized in part to a pasty mass. After this had been spread on a porous tile, it yielded a product which could be recrystallized from alcohol and gave transparent plates; m. p., 37.5°.

Benzylated Urea.—Sym-dibenzylurea, m. p. 167°, was obtained in 69.2% yield by heating 2 equivalents of benzylamine with 1 equivalent of urea for 2 hours at 160–170°, and working up the product from alcohol.

Monobenzylurea, m. p., 146.6° , was produced along with dibenzylurea when urea and benzylamine were heated at $160-170^{\circ}$ in molecular proportions. Two g. of benzylurea heated at $160-170^{\circ}$ for 3 hours gave off ammonia, and 0.6 g. of pure dibenzyl was obtained from the product.

When urea was refluxed with benzylamine in aqueous solution, benzylurea was formed (95.8% yield, calculated from urea), but no dibenzylurea was produced even when a large excess of the amine was present. Unlike phenylurea, benzylurea is not

converted into dibenzylurea by boiling in water. Even long-continued boiling alone and in the presence of benzylamine and of dil. sulfuric acid were without effect, except that in the latter case an odor of isonitrile was noticed.

Reactions with Secondary Amines.—When urea was refluxed in aqueous solution with methylaniline, no ammonia was given off and no new substance was isolated from the mixture. No product was isolated from the mixture which resulted from the heating together of dibutylamine hydrochloride and urea. The 1,1-disubstituted ureas have been obtained (in poor yield) by boiling urea with aqueous solutions of the hydrochlorides of methylaniline and ethylaniline.

A mixture of 15.3 g. of ethylaniline hydrochloride and 6 g. of urea was refluxed in 50 cc. of water for 5 hours. Considerable oil separated. The material was extracted with ether and the extract was shaken with dil. hydrochloric acid for the removal of amine. Some of the substituted urea was also evidently removed, for the ether solution, dried and evaporated, yielded only about 0.1 g. of oil which crystallized after long standing. Recrystallized from ligroin this yielded pure unsym-ethylphenylurea, as white, lustrous, thin plates, m. p., 62°, identified by mixed melting point with a sample prepared from potassium cyanate and ethylaniline hydrochloride.

A mixture of 7.4 g. of methylaniline hydrochloride and 2 g. of urea in 20 cc. of water was refluxed for 9 hours. Considerable oil separated. The ether extract, when dried and allowed to evaporate, yielded about 1 g. of crystals, which when recrystallized from ligroin gave thin plates, m. p. 150°, that were identified as *unsym*-methylphenylurea by mixed melting point with a synthetic sample.

Summary

Urea may be used for the preparation of mono-substituted ureas from primary amines, by heating at 160° or by boiling in aqueous solution. The monosubstituted ureas, in the same way, are equivalent to the isocyanate for purposes of synthesis and yield *sym*-disubstituted ureas. The syntheses have been studied with the phenyl compounds and with a number of substances in the aliphatic series.

Certain secondary amines react with the nascent isocyanic acid from urea to form *unsym*-disubstituted ureas, but the yields are poor.

Unsymmetrical disubstituted ureas and symmetrical disubstituted ureas in which the groups are alike, dearrange in only one fashion. Symmetrical disubstituted ureas in which the substituent groups are different dearrange in two modes. Striking evidence is found in the fact that unsymethylphenylurea yields carbanilide when heated.

Cambridge 39, Massachusetts

[CONTRIBUTION FROM THE FUEL SECTION, GENERAL MOTORS RESEARCH CORPORATION, AND THE RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A NEW METALLO-ORGANIC COMPOUND: DIPLUMBIC HEXA-ETHYL¹

By Thomas Midgley, Jr., Carroll A. Hochwalt and George Calingaert Received May 10, 1923

Introduction

Two ethyl lead compounds are reported in the literature.

Tetra-ethyl lead was prepared by P. Pfeiffer by the action of lead chloride on ethylmagnesium iodide, according to the equation: $4C_2H_5MgI + 2PbCl_2 \longrightarrow Pb + Pb-(C_2H_5)_4 + 2MgI_2 + 2MgCl_2$. Löwig reported the preparation of "hexa-ethyl lead" by interaction of sodium-lead alloys and ethyl iodide. However, the formulas given by Löwig are antiquated, as they refer to water as HO. Löwig also considered lead as having an atomic weight of 103, and it is impossible to ascertain whether he assumed the formula for his compound to be PbEt3 or Pb2Et6. At any rate, his statement is not confirmed either by a molecular-weight determination or by an analysis for lead. Moreover, a more recent experimenter duplicated Löwig's work, and showed that the product obtained by Löwig was actually impure tetra-ethyl lead, the same as had been obtained in the meanwhile by Buckton by interaction of lead chloride and zinc ethyl, according to the equation, $2PbCl_2 + 2ZnEt_2 = Pb + PbEt_4 + 2ZnCl_2$. To quote Ghira, "I think it is not too much to presume that at the present time no lead compounds of the type PbX_3 or Pb_2X_5 have ever been reported, studied or isolated."

An exhaustive study of organic compounds of tetravalent lead has been made during the past few years by E. Krause and his co-workers. Krause prepared all his lead alkyls by Pfeiffer's method, and reported⁶ the following constants for Pb(C₂H₅)₄: b. p., 83° (14 mm.); d¹⁸, 1.6591.

The method used by Krause, namely, the decomposition of an alkyl or aryl magnesium halide by lead chloride, always yields a tetra-alkyl lead compound when an alkyl halide is used. However, using aryl halides and an insufficient amount of lead chloride, Krause was able to prepare a series of compounds of the type, PbX₃ or Pb₂X₆, which he considers as corresponding to trivalent lead.⁷

Experimental Part

In the work done by the authors of this paper, 65 g. of triethyl lead chloride, covered with 100 cc. of distilled water, was stirred with 40 cc. of 5 N sodium hydroxide solution until all had dissolved. The triethyl lead hydroxide formed was precipitated from this solution by the addition of 200 cc. of 5 N sodium hydroxide solution, and was separated; 60 g. of this hydroxide was dissolved in 200 cc. of 95% ethyl alcohol and electrolyzed with lead electrodes, using a current density of 0.01 amperes per sq.

- ¹ Read at the New Haven Meeting of the American Chemical Society, April, 1923.
- ² Pfeiffer, Ber., 37, 1126 (1904).
- ³ Löwig, J. prakt. Chem., **60**, 304 (1853).
- ⁴ Ghira, Gazz. chim. ital., 24, 1, 42 (1894).
- ⁵ Buckton, Ann., 109, 222 (1859).
- 6 Krause, Ber., 49, 1415 (1916).
- ⁷ Krause, ibid., 55, 888 (1922).

cm. An oil was formed at the cathode, and much gas evolved at the anode. This oil was heavy and insoluble in alcohol, so that it collected at the bottom of the cell. The reaction is expressed by the following equations: $Pb(C_2H_5)_3OH = Pb(C_2H_5)_3^+ + (OH)^-$; $2Pb(C_2H_5)_3^+ + 2\Theta = Pb_2(C_2H_5)_6$.

Properties of the Oil.—The oil so obtained is yellowish and easily decomposed by air, giving a yellowish powder that darkens rapidly; d., 1.94. It distilled with steam without decomposition, but very slowly, in the ratio of 1 cc. of diplumbic hexa-ethyl, $Pb_2(C_2H_5)_6$, to 25–30 cc. of water. It could not be distilled directly without decomposition, but under 2mm. pressure it boiled at about 100°. It did not freeze at —80°.

Analysis.—A sample of the oil was analyzed for lead by the method of Krause.⁸ Subs., 0.235: PbBr₂, 0.291. Calc. for C₁₂H₃₀Pb₂: Pb, 70.4; calc. for C₈H₂₀Pb: Pb, 64.1. Found: 69.8.

The molecular weight was determined by the freezing-point lowering of benzene, using 5.10° as the cryoscopic constant for benzene, this being the value used by Krause for all lead compounds.

Subs., 0.6285, 0.0482, 0.0212, 0.0182: benzene, 9.184, 13.35, 11.48, 14.44; Δt , 0.600, 0.040, 0.032, 0.022. Calc. for $Pb_2(C_2H_\delta)_6$: mol. wt., 588; calc. for $Pb(C_2H_\delta)_7$; 294. Found: 582, 460, 294, 292.

Thus, diplumbic hexa-ethyl, like the corresponding aryl compounds⁷ is dissociated in 2 PbX₃ groups in dilute solutions, but exists as Pb₂X₆ at higher concentrations.

This shows one more similarity between organic lead and tin compounds, as it was usually considered that the last one only is able to give organic compounds containing a chain of 2 atoms of the metal. However, the easy dissociation shown by these compounds is very different from what is observed with carbon chains, and leaves but little hope as to the possibility of preparing longer chains of lead atoms.

An attempt was made to prepare the chlorine derivative of this compound. Since tetra-ethyl lead reacts with hydrochloric acid to form ethane and triethyl lead chloride, it was hoped that the hexa-ethyl compound might react similarly to give a substance, $Pb_2(C_2H_5)_5Cl$. Such is not the case; instead, the Pb-Pb linkage is apparently broken, giving as the main products of the reaction lead triethyl chloride $Pb(C_2H_5)_3Cl$, and lead chloride, while gas is given off. The reaction may probably be written as follows: $Pb_2(C_2H_5)_6 + 3HCl = Pb(C_2H_5)_3Cl + PbCl_2 + 3C_2H_6$.

Summary

Inasmuch as all organic lead compounds of the type PbX₄ are able to yield derivatives of the general formulas PbX₃Cl and PbX₃OH, a method has been developed by which the corresponding Pb₂X₆ compounds can be obtained readily.

⁸ Krause, Ber., 49, 1130 (1916).

It has been shown that such compounds are represented by the formula Pb_2X_6 in pure state or in concentrated solutions, and by PbX_3 in very dilute benzene solutions.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE SUGAR CONTAINED IN TUBERCULINIC ACID, THE NUCLEIC ACID OF TUBERCLE BACILLI

By Elmer B. Brown and Treat B. Johnson¹ Received May 11, 1923

In previous papers by the authors² a description has been given of the method used for separating tuberculinic acid from tubercle bacilli, and also the nature of the pyrimidines which function in this acid. On the basis of new data obtained in our research we concluded that tuberculinic acid containing the pyrimidines, thymine and cytosine, but no uracil, resembles in its chemical characteristics a nucleic acid of animal origin, thereby establishing the natural group to which the tubercle bacillus is to be assigned. It is also known that the carbohydrates contained in plant and animal nucleic acids are characteristic of each group and differ in the two acids, hexose occurring in the acid of animal origin and pentose in the plant variety. Hence, an accurate knowledge of the sugar contained in tuberculinic acid would serve as a check on the above classification of the tubercle bacillus which is based on the results of a pyrimidine analysis.

The literature of the chemistry of tubercle bacillus reveals the fact that the carbohydrate phase of the work has received little attention at the hands of previous investigators, notwithstanding the fact that one of the first of them, Hammerschlag³ recognized its importance. He was able to detect a reducing sugar in defatted bacilli, but thought he was dealing with cellulose. De Schweinitz and Dorset⁴ were of the same opinion in regard to the nature of the carbohydrate contained in this material. Levene⁵ isolated a carbohydrate of a glycogen-like nature as an impurity of the nucleic acid from tubercle bacilli, but did not further investigate it beyond the point of ascertaining that it formed a soluble copper salt which permitted its separation from the insoluble copper nucleate.

Bendix⁶ was the first investigator to report the finding of a sugar complex in the nucleoprotein obtained from the tubercle bacillus. He characterized his product as a pentose, but gave no details as to the method employed in its isolation, nor any characteristic chemical tests in support of his conclusion. The only other investigator, so far

¹ This work was done with the aid of a grant from the Committee on Medical Research of the National Tuberculosis Association. The tubercle bacilli used in this research were furnished gratuitously to the writers by Parke, Davis and Co. and the Mulford Co. We take this opportunity to express appreciation of their coöperation and interest in our research.

² Brown and Johnson, J. Biol. Chem., 54, 721, 731 (1922).

³ Hammerschlag, Monatsh., 10, 9 (1892).

De Schweinitz and Dorset, This Journal, 17, 605 (1895).

⁵ Levene, J. Exp. Med., 6, 135 (1901).

⁶ Bendix, Deut. med. Wochschr., 1901, 16.

as the writers are aware, to report the finding of a sugar in the nucleoprotein from the tubercle bacillus was Goris⁷ who claims to have found a hexose. The nucleoprotein was obtained from the defatted bacilli by extraction with water and precipitation with alcohol. Chemical data supporting this conclusion are also lacking.

Two other investigators working on tubercle bacilli have found sugars in the extracts of different solvents used on this material. Kozniewski⁸ found that acetone extracted a substance from tubercle bacilli which, when treated with dil. mineral acids was decomposed with the formation of an inactive reducing sugar. Agulhon and Frouin⁹ by the use of alcohol were able to extract a substance that yielded dextrose. These findings are of interest in showing the different parts of the bacillus from which the presence of sugars has been reported.

It is readily seen that the previous work on the carbohydrates of the tubercle bacillus gives very little accurate information in regard to the nature of the sugar functioning in this organism. Beyond the fact that a few investigators were able to find evidence of the presence of reducing sugars in different fractions of the tubercle bacillus, no conclusive results on the nature of these products have been obtained. Since the methods used for the identification of the different products were of a general nature and the material very complex, naturally the results obtained by the different investigators were incomplete and contradictory.

As a part of their investigation of the "Chemistry of the Tubercle Bacillus," which has been in progress in this Laboratory during the past 2 years. the writers have now been able to investigate the nature of the sugar contained in tuberculinic acid. After subjecting this nucleic acid to all the purification processes commonly used for the purification of other nucleic acids, a product was finally obtained which showed a constant content of nitrogen and phosphorus. Small portions of this material were used to ascertain qualitatively the nature of the decomposition products of the sugar, when subjected to acid hydrolysis. These tests showed that relatively large amounts of both formic and levulinic acids were produced and only very small amounts of furfuraldehyde. With this information in hand, greater amounts of tuberculinic acid were employed and the above products isolated and identified. Since hexose sugars yield on acid hydrolysis the above decomposition products and the pentoses under the same conditions yield only furfuraldehyde, the sugar functioning in tuberculinic acid is therefore definitely shown to be a hexose. The new data obtained by us are in complete accord with the results of our former work in which we found that thymine and cytosine were the only pyrimidines contained in tuberculinic acid, and show conclusively that the decomposition products of this nucleic acid are identical with those of known acids of animal origin, and different from those of the plant type in both their pyrimidine and sugar content.

Goris and Liot, Ann. inst. Pasteur, 34, 497 (1920).

⁸ Kozniewski, Bull. intern. acad. Sci. Cracovie, Series A, p. 942, 1912.

² Agulhon and Frouin, Bull. soc. chim. biol., 1, 176 (1919).

In the experimental part of this paper is given a complete description of the behavior of tuberculinic acid when subjected to hydrolysis, and a report of our examination of the hydrolysis products produced by the decomposition of the sugar.

Experimental Part

The Purification of Tuberculinic Acid.—The nucleic acid used in this work was separated from tubercle bacilli by the application of our method, described in our previous publications² to a large amount of human and bovine tubercle bacilli which had previously been defatted with toluene.

The crude tuberculinic acid, 8.4 g. obtained from 810 g. of dry tubercle bacilli, was further purified by solution in 1% sodium hydroxide solution, addition of acetic acid until the solution was neutral, then picric acid as long as a precipitate was formed and finally acetic acid until the mixture was distinctly acid to litmus. To the filtered solution hydrochloric acid was then added until a faint turbidity was produced and the nucleic acid precipitated from the solution by the addition of twice its volume of 95% alcohol. The precipitate was separated from the solution by a high-speed centrifuge, washed with 50% alcohol containing hydrochloric acid and finally with 95% alcohol, absolute alcohol and with anhydrous ether. The dry product was a light gray powder and contained 8.11% of phosphorus and 11.3% of nitrogen. This material was then dissolved in dil. potassium hydroxide solution, the solution poured into 6 times its volume of absolute ethyl alcohol, and the precipitated potassium salt separated by means of the centrifuge. This was then washed with absolute alcohol and dried with ether. A granular powder, slightly yellow in color, was obtained. The salt was again dissolved in water and converted into the copper salt by acidification with acetic acid, filtration, addition of hydrochloric acid until an opalescence was produced and, finally, addition of 10% copper chloride solution. The copper salt was purified and converted into the free nucleic acid according to the directions of Levene, 10 using 5% hydrochloric acid. Analysis showed that the percentages of nitrogen and phosphorus had not changed and that we had a product which further treatment did not alter.

The Decomposition Products of the Sugar Produced on Hydrolysis of Tuberculinic Acid with Hydrochloric Acid.—One g. of tuberculinic acid was placed in a 500cc. distilling flask with 250 cc. of hydrochloric acid (d., 1.06) and the mixture distilled from an oil-bath at 150°. At intervals, when 25 cc. of distillate had passed over, an equal volume of hydrochloric acid (d., 1.06) was added maintaining approximately the same strength of solution. The distillation was continued for 7 hours, during which about a liter of distillate was collected. The solution did not boil smoothly, but occasionally foamed and super-heated, and on one occasion boiled over, a few drops reaching the bulk of the distillate before the receiver could be changed.

To the distillate an excess of phloroglucine dissolved in hydrochloric acid was added and the mixture heated at 80° to 85° for 2 hours and then allowed to stand overnight. The phloroglucide precipitate was collected on an asbestos mat in a Gooch crucible that had been previously dried to constant weight at 98°, washed with water and again dried to constant weight at the same temperature. This weighed 0.024 g. Since Osborn and Harris¹¹ under the same conditions obtained 0.252 g. of this product from 1 g. of triticonucleic acid from wheat, it is readily seen that the 2 acids differ markedly from each other in the amount of furfuraldehyde produced on hydrolysis. Steudel, 12 working

¹⁰ Levene, J. Biol. Chem., 48, 177 (1921).

¹¹ Osborn and Harris, Z. physiol. Chem., 36, 85 (1902).

¹² Steudel, *ibid.*, **56**, 212 (1908).

with thymus nucleic acid, also obtained furfuraldehyde, but in amounts somewhat smaller than the quantity produced from tuberculinic acid. The results obtained in the case of tuberculinic acid agree very closely with the results obtained by other investigators working with animal nucleic acids and differ materially from the results obtained when the plant acids were examined.

The solution remaining from the preceding experiment was utilized to ascertain whether levulinic acid was produced as a hydrolytic product of tuberculinic acid. The distillation was continued to dryness and the residue exhaustively extracted with ether, the ether extract poured through a dry filter paper and the ether then expelled by distillation. The gummy residue was heated on the hot plate for 2 hours to expel any hydrochloric or formic acids that it might contain, dissolved in 25 cc. of water and finally filtered from a small amount of insoluble material. Preliminary tests on 1cc. portions of this solution showed that it gave a strong iodoform reaction, as well as a deep red color when sodium nitroprusside and a few drops of sodium hydroxide solution were added, the color changing to violet after the addition of an excess of acetic acid. These tests, especially the latter, are characteristic of levulinic acid. The remainder of the solution was digested for 1 hour with an excess of zinc oxide according to the directions of Wehmer and Tollens¹³ in order to prepare the zinc salt. After decolorization with animal charcoal the filtered solution was evaporated to a small volume, when a precipitate began to separate; as the solution cooled, more was obtained. This precipitate was crystalline, showing 6-sided crystals when viewed under the microscope, and was identical in appearance with the zinc salt prepared from levulinic acid. The solution was evaporated to dryness, the residue washed with a mixture of equal parts of absolute alcohol and ether, dissolved in water and silver nitrate solution was added. A precipitate was obtained but in too small amount for a silver determination. These tests show conclusively that levulinic acid is produced on acid hydrolysis of tuberculinic acid.

The Isolation of Levulinic Acid from Tuberculinic Acid.—To 3.8 g. of tuberculinic acid in a 300cc. round-bottom Pyrex flask, 30 cc. of water and 10 cc. of concd. sulfuric acid were added and the mixture was heated in an oil-bath at 125° for 25 hours under a return condenser. At the end of this time 50 cc. of water was added and the solution distilled until 50 cc. had passed over. This distillate, which contained formic acid was saved, as described below.

The solution remaining in the hydrolysis flask was exhaustively extracted with ether, the ether extract poured through a dry filter and the ether distilled on a water-bath. The residue was allowed to remain on the steam-bath to dispel traces of water and formic acid. A viscous sirup was obtained, weighing 0.5 g. and composed chiefly of levulinic acid. This amount figured in terms of its hexose equivalent corresponds to 37.5% of the weight of tuberculinic acid used. The crude residue was dissolved in water, exactly neutralized with sodium hydroxide solution, and silver nitrate solution added in excess. A beautiful precipitate of the silver salt of levulinic acid was obtained. This was recrystallized once from water and dried at 100°.

Analysis. Subs., 0.1923: Ag, 0.094. Calc. for C₈H₇O₃Ag: Ag, 48.43. Found: 48.88. In other words, it was established that this compound was identical in every respect with the silver salt prepared from levulinic acid.

The Identification of Formic Acid.—The distillate obtained as described above was strongly acid to litmus, and when a few cubic centimeters was warmed with silver nitrate solution a silver mirror was obtained. A black deposit of mercury was immediately obtained when a crystal of mercurous nitrate was added and the solution warmed. A portion of the solution when neutralized with sodium hydroxide and treated with ferric chloride solution gave the characteristic red color when boiled, showing the formation

¹³ Wehmer and Tollens, Ann., 243, 314 (1887).

of ferric formate. When 30 cc. of the distillate was neutralized with sodium hydroxide the solution, then made acid to litmus with hydrochloric acid, and a solution of mercuric chloride added and the mixture digested on the water-bath, a white precipitate soon began to form. A large amount of calomel was obtained, covering the entire bottom of the beaker. These results show conclusively that the acid contained in the distillate was formic acid.

The Quantitative Determination of the Pyrimidines.—The solution remaining from the ether extraction was worked for the pyrimidines according to the directions given in one of our previous papers.² After the removal of sulfuric acid with barium hydroxide, and the purines with silver sulfate in acid solution, the pyrimidines were precipitated in the usual manner as silver salts. These salts were decomposed with hydrogen sulfide and the cytosine removed as the phosphotungstate. After decomposition of this salt with barium hydroxide the cytosine was isolated as the base; 0.37 g. was obtained, corresponding to 9.7% of the weight of nucleic acid used.

The filtrate left from the phosphotungstate precipitation was freed from this reagent with barium hydroxide, the barium removed in the usual way and the solution evaporated to dryness. The residue was taken up in water and filtered from a small amount of insoluble material and the solution again evaporated to dryness and weighed. The crude thymine weighed $0.45~\rm g.$, corresponding to 11.8% of the weight of the nucleic acid used. All of our solutions failed to respond to tests for uracil.

Summary

- 1. It has been shown that the sugar functioning in tuberculinic acid is a hexose. This was proven by identification of levulinic and formic acids as products of its hydrolysis.
- 2. A new analysis for pyrimidines in tuberculinic acid has been made and results have been obtained which are identical with those reported in our previous publication.²

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTION OF ULTRAVIOLET LIGHT UPON DIKETONES

By C. W. PORTER, H. C. RAMSPERGER AND CAROLYN STEEL

Received May 16, 1923

In aqueous solution benzil is converted into benzilic acid by warming it with an alkali. The reaction is rapid and practically quantitative. It has been reported that the same rearrangement occurs slowly in the absence of alkali when benzil, in moist ether, is exposed to sunlight. Under similar treatment benzil in alcohol yields benzoic acid and benzoin.²

This investigation was undertaken to determine the action of radiant energy of short wave lengths upon aqueous and alcoholic solutions of benzil and the corresponding aliphatic diketone, diacetyl.

Preliminary tests were made with saturated aqueous solutions of benzil. The solutions were placed in open beakers with the liquid surfaces 18 cm. below a 110-volt quartz mercury-vapor lamp. Samples were withdrawn

¹ Klinger, Ber., 19, 1868 (1886). Lachman, This Journal, 44, 330 (1922).

² Ciamician and Silber, Ber., 36, 1575 (1903).

every 3 hours and titrated with sodium hydroxide solution. There was a gradual development of acid but an exposure of at least 30 hours was required to secure enough of the product for identification. Benzoic acid was the principal product.

Because of the slight solubility of benzil in water (0.33 g. per liter at 20°) mixtures of alcohol and water were used in the later experiments, and since ethyl alcohol is oxidized by the oxygen of the air under the influence of the ultraviolet light, blank determinations with the solvent alone were made under the same conditions. The acetic acid which developed in the blank tests (100cc. portions) amounted to approximately 1.2×10^{-6} moles per hour. Within 12 hours the benzil in 66% alcohol was completely converted into other products. The solvent was then removed by evaporation. By repeated extractions with hot water we obtained from the yellow tarry residue a mixture of colorless crystals. Approximately 80% of this crystalline part of the product was benzoic acid. The remainder was salicylic acid.

The mechanism for the production of these acids from benzil has been determined. The first step is hydrolysis of the diketone resulting in the production of benzoic acid and benzaldehyde. Atmospheric oxidation of benzaldehyde to benzoic acid is catalyzed by ultraviolet light and salicylic acid is formed from benzoic acid under the same conditions. A qualitative test for salicylic acid can be obtained when an alcoholic solution of benzoic acid is exposed to the ultraviolet light for less than an hour. When air was excluded by making the exposures in quartz flasks in an atmosphere of nitrogen no salicylic acid was formed. Under these conditions the oxidation of benzaldehyde was prevented, also, and the aldehyde appeared as one of the final products. Benzoin was produced in considerable quantities in the oxygen-free samples but we have not yet determined whether the production of benzoin is due entirely to reduction of benzil by alcohol or is due in part to a condensation of benzaldehyde.

In order to determine whether benzilic acid could be an intermediate product we exposed both water and alcohol solutions of pure benzilic acid. The solutions became cloudy in the first half hour of exposure. Two products were isolated. One was benzopinacol, $(C_6H_5)_2$. COH. COH. $(C_6H_5)_2$, and the other benzophenone. These products were never obtained from benzil.

Experimental Part

Benzil in Dry Benzene.—Several 50cc. portions of a 1% solution of benzil in dry, oxygen-free benzene were placed in quartz flasks, boiled to

³ The test for benzil was made by boiling the solution with an alkali, evaporating to dryness, and treating the residue with concd. sulfuric acid. Under this treatment, a mere trace of benzil yields benzilic acid in sufficient quantity to impart a red color to the sulfuric acid.

expel air from the solution, and the air of the flasks was replaced by pure nitrogen. Mercury seals were placed about the necks of the flasks. The solutions were exposed for 1 to 7 hours at a distance of 20 cm. from a 220-volt mercury arc. They acquired a light straw color as does pure benzene alone. When the solution was evaporated to dryness the benzil was recovered unchanged.

Benzil Vapor Exposed.—When exposed at a temperature of 200° in an evacuated flask for 6 hours, 0.2755 g. of benzil yielded 18 cc. of carbon monoxide (0°, 760 mm.) and a corresponding quantity of benzophenone. A flask containing benzil protected from the light by tin foil was kept in the same thermostat during the same interval of time. There was no thermal decomposition of the benzil.

Benzil in Water.—Several 50cc. portions of an aqueous solution of benzil (0.3 g. per liter) were exposed in quartz flasks in the presence of air. The increase in acidity during 30 hours is indicated in the following table.

TABLE I

Increase in Acidity of an Aqueous Solution of Benzil upon Exposure to Ultraviolet Light

Benzil in Alcohol and Water.—A stock solution was prepared by dissolving 2 g. of benzil per liter in 66% ethyl alcohol; 100cc. portions of this solution were exposed in quartz flasks. At the same time 100cc. portions of the pure solvent were exposed. At each interval indicated in the following table a benzil solution and a blank were withdrawn and titrated. The amount of the base reported is the difference between the two titrations.

TABLE II

EXPOSURE OF BENZIL IN WATER AND ALCOHOL

Time, hours....... 1 2 3 4 5 6 7 8 9 10 0.062 N NaOH, ec... 4.28 6.30 8.70 10.72 13.35 15.40 16.50 17.20 17.82 18.06

Assuming that 2 mols. of acid are derived from each mol. of benzil, this represents only a little more than 50% conversion, but the benzil had completely disappeared. Approximately half of it was converted into a resinous product, which we have not identified, and half was converted into benzoic acid. Part of the benzoic acid was oxidized to salicylic acid. The crystalline product was usually 80% to 90% benzoic acid and 20% to 10% salicylic acid.

Exposures in the Absence of Air.—Solutions of benzil in aqueous alcohol were exposed to a 220-volt lamp for 8 hours in the absence of air. A white precipitate formed and was identified as benzoin (m. p., 132–134°). Benzoic acid was isolated as in previous cases, but no salicylic acid was produced. The pure solvent (66% alcohol) under nitrogen yielded no acetic acid. Some hydrogen was produced from both the pure solvent

and the benzil solution. This is due to the decomposition of the ethyl alcohol into acetaldehyde and hydrogen. Alcohol thus acts as a reducing agent producing benzoin from benzil.

Benzilic Acid Exposed.—Benzilic acid, when dissolved in 50% alcohol and exposed to ultraviolet light, is converted into benzopinacol. When air is present benzophenone is produced also; but in the absence of air benzophenone is reduced to benzopinacol so rapidly that it never appears as a final product of the reaction.

Diacetyl in Water.—A stock solution of diacetyl was prepared by dissolving 2 g. of the diketone in 1 liter of water; 100cc. portions of this solution were exposed at a distance of 14 cm. from a 220-volt lamp. The substance was converted into acetic acid and acetaldehyde. The rate of acid formation is indicated by the following measurements.

TABLE III

Exposure of Diacetyl in Water

Time, hours	1	2	3	4	5	6	7	8	9	10
0.01 N NaOH, cc	70	100	118	130	138	144	148	151	152	153

Diacetyl Vapor.—A quartz flask having a capacity of 125 cc. was filled with diacetyl vapor at 100° and 1 atmosphere pressure and exposed to ultraviolet light. Gas was evolved at the rate of 8 cc. per minute. The gas was collected over mercury and analyzed. It was found to be carbon monoxide (2 vols.) and ethane (1 vol.).

Summary

Under the influence of ultraviolet light, benzil in the vapor state is decomposed into carbon monoxide and benzophenone when the temperature is 200° or above.

In dil. alcohol, in the absence of air, it is partly hydrolyzed to benzoic acid and benzaldehyde, but a portion of it is reduced by the alcohol to benzoin.

In aqueous alcohol in contact with air it is converted into benzoic acid. Further oxidation of the benzoic acid gives some salicylic acid.

Benzilic acid is not formed in solutions of benzil. The decomposition products of benzilic acid, namely, benzopinacol in the absence of oxygen, and benzophenone and benzopinacol in the presence of oxygen, were never found in the exposed benzil solutions.

Under the influence of ultraviolet light, diacetyl vapor yields ethane and carbon monoxide.

An aqueous solution of diacetyl yields acetic acid and acetaldehyde.

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⁴ Berthelet and Gaudechon, Compt. rend., 153, 383 (1912).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

DERIVATIVES OF ANTHRAQUINONE. REACTIONS OF ANTHRAQUINONE SULFONIC ACIDS WITH MERCAPTANS¹

By W. S. Hoffman and E. Emmet Reid Received May 16, 1923

In a recent paper by Reid, Mackall and Miller² it has been shown that sulfonic acid groups in the α -position in anthraquinone are readily replaced by mercaptan residues to form anthraquinone thio-ethers, thio-ether sulfonic acids, and dithio-ethers, $C_{14}H_7O_2.SR$, 1,5- and 1,8-RS. $C_{14}H_6O_2.SO_3Na$ and 1,5- and 1,8- $C_{14}H_6O_2(SR)_2$.

The present investigation was undertaken to determine the best conditions for this reaction and to extend it to other mercaptans, particularly those of other types.

The speed of the reaction depends on the concentration of the sodium salt of the mercaptan and, hence, on account of the weakness of mercaptans as acids, is increased by excess of alkali. Alkali, however, tends to salt out the sodium anthraquinone sulfonate. Practically the maximum yield is reached with 4 equivalents of alkali and 4 hours' heating.

Previous work had shown that the reaction takes place with primary aliphatic mercaptans but not with aromatic. Benzyl mercaptan has been tried and has been found to work well, yielding well-characterized derivatives. p-Nitrobenzyl mercaptan reacts rapidly but the products are complex, extremely insoluble and difficult to handle, and so were discarded.

No difficulty was found in obtaining good yields of characteristic reaction products with isopropyl mercaptan, but the corresponding sulfones are obtained in small yield, if at all, since the —SCH(CH₃)₂ group is readily oxidized to —SO₃H and the sulfonic acids are obtained quantitatively if the oxidation is vigorous. In the case of mixed dithio-ethers an isopropyl group is oxidized to the sulfonic acid while, with the other, oxidation stops at the sulfone: RS.C₁₄H₆O₂.SCH(CH₃)₂ \longrightarrow RSO₂.C₁₄H₆O₂.SO₃H. Small yields of sulfones may be obtained from the 1- and the 1,5-, but none from the 1,8-dithio-ethers containing an isopropyl group. Monothio-ethylene glycol has been found to react normally, its reaction rate being greater than those of the simple mercaptans on account of its solubility in water and low volatility. The resulting hydroxy-thio-ethers are slightly soluble in water and readily act with hydrosulfite.

Ethylene mercaptan was found to react rapidly but the products are complicated and could not be purified; the principal one from the monosulfonic acid seemed to be the disulfide, C₁₄H₇O₂.SC₂H₄S.SC₂H₄S.C₁₄H₇O₂.

¹ From a dissertation presented by W. S. Hoffman in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Reid, Mackall and Miller, This Journal, 43, 2104 (1921).

1.5-Anthraquinone-butyl-sulfone-sodium sulfonate, C4H9SO2C14H6O2.-SO₃Na, was prepared by the oxidation of the corresponding thio-ether with fuming nitric acid. It is quite soluble in water; it separates from hot water with half a molecule of water of crystallization and from cold with 1 molecule. As previously shown, the thio-ether anthraquinone sodium sulfonate reacts with mercaptans, but on account of its extremely slight solubility even in boiling water, the reaction is very slow. Possibly on account of its far greater solubility, possibly partly on acount of greater reactivity, the sulfone-sulfonate mentioned above reacts extremely rapidly with mercaptans in hot alkaline solution to give sulfone-thio-ethers, 1.5-C₄H₉SO₂.C₁₄H₆O₂.SR, which appear as precipitates the instant that the mercaptans are added to the mixture. The yields are practically quantitative. In fact the reaction may advantageously be used for the identification of mercaptans. The melting points of the butyl sulfone-alkylthio-ethers so formed are definite but it is better to oxidize with fuming nitric acid to the mixed disulfones. These are particularly easy to purify and have good melting points. A number of these are given in previous article.3 Satisfactory results may be obtained with very small quantities of the mercaptans.

The great reactivity of the butyl-sulfone-anthraquinone sodium sulfonate toward mercaptans suggested that it might react with some compounds with which the sodium-anthraquinone sulfonates do not react. This has proved to be true with thiophenol which reacts at a satisfactory rate to give a good yield of butyl-sulfone-anthraquinone-thiophenol ether, $C_4H_9SO_2$.- $C_{14}H_6O_2$.S C_6H_5 , but the reaction does not go as fast and the yield is not as good as with the aliphatic mercaptans. p-Nitrothiophenol was tried in a similar manner. No product separated from the alkaline solution, which may be explained by the probable formation of some sort of sodium salt. After 4 hours' boiling the mixture was acidified and gave a brown solid which proved difficult to purify and was discarded. The reaction evidently takes place, but not smoothly.

It was thought that perhaps alcohols might react to give oxygen ethers. Butyl alcohol was added to the boiling alkaline solution of butyl-sulfone-anthraquinone sodium sulfonate and boiled for some time, but there was no indication of a reaction.

Experimental Part

Preparation of Butyl-anthraquinone Thio-ether. The effect of time, dilution and quantity of alkali upon the preparation of this substance as described in the preliminary article has been studied. In each experiment 3 g. of the sodium anthraquinone sulfonate was used and 1.25 equivalents of butyl mercaptan in boiling solution. The product was filtered on a small Büchner funnel, well washed with hot water, dried and weighed.

³ Ref. 2, p. 2113.

TAB	le I				
Volume, 150 cc.	4 ec	q. NaO	H	•	
Time, hours	1	2	4	6	8
Yield, %	59	75	78	84	85
Tab	le II				
4 hours. 4	eq. N	aOH			
Volume, cc			150	300	600
Yield, %	. 86	.4	78.5	57.8	24.5
TABL	E III				
4 hours. Vo	olume,	75 cc.			
Eq. NaOH	0	1	2	4	8
Vield. %	0	67	80	86	85

The best conditions are 4 hours' boiling, 25 parts of water and 4 equivalents of sodium hydroxide.

Reactions with Benzyl and p-Nitrobenzyl Mercaptans

Preparation of Mercaptans.—Benzyl mercaptan was prepared by a slight modification of the general method given by Märcker. One and a half moles of crystallized sodium sulfide was melted at 90° on a water-bath and was saturated with hydrogen sulfide. To this was added an equal volume of ethyl alcohol, and the mixture was resaturated with hydrogen sulfide; finally a mole of benzyl chloride dissolved in alcohol was added. The mixture was allowed to stand in the cold, with frequent shaking for 4 days, kept cold if necessary with running water to prevent as much as possible the oxidation of the mercaptan to the disulfide and the formation of the monosulfide, both of which reactions take place readily at high temperatures. The mixture was then diluted with water, the mercaptan separated and distilled under reduced pressure.

We were unable to prepare p-nitrobenzyl mercaptan in this way, although Strakosch⁵ maintains that he did. Nor was the method proposed by Price and Twiss⁶ found successful. The method finally employed was that of Waters⁷. p-Nitrobenzyl thiocyanate (made by the action of potassium thiocyanate on an alcohol-water solution of p-nitrobenzyl bromide) was dissolved in cold alcohol and saturated with hydrogen chloride, and allowed to stand cold for 8 days. Upon the addition of water, p-nitrobenzyl thiocarbamine ester (p-NO₂C₆H₄CH₂SCONH₂) separated, and was removed, dissolved in alcohol, and heated with a little more than 1 equivalent of zinc acetate. The cooled mixture was poured into a large quantity of water, precipitating the zinc p-nitrobenzyl mercaptide, which was separated, and decomposed with concd. hydrochloric acid, liberating the free mercaptan that melted when pure at 52°.

Reaction of Mercaptans.—Benzyl mercaptan was caused to react with 1-anthraquinone sodium sulfonate, with 1,5- and 1,8-disodium sulfonates and with the thioether sodium sulfonates prepared by Reid, Mackall and Miller. The reactions were slower than with butyl mercaptan, so the time of heating was lengthened to 8 to 10 hours. The thio-ethers so obtained were converted to sulfones by solution in glacial acetic acid, addition of slight excess of concd. water solution of chromic anhydride and heating for half an hour. As this mixture cooled the sulfones separated as yellowish-white crystals which were quite pure.

⁴ Märcker, Ann., 136, 76 (1865).

⁵ Strakosch, Ber., 5, 692 (1872).

⁶ Price and Twiss, J. Chem. Soc., 95, 1726 (1909).

⁷ Waters, Dissertation, Munich, 1905.

Properties and analyses of the products are given in tabular form. The thio-ethers were recrystallized from solvent naphtha and the sulfones from acetic acid. The salts in Table V are orange-colored.

Table IV
Benzyl-anthraquinone Thio-ethers

		Sulfur						
	Formula	М. р. °С.	Cale. %	Found %	Color			
1-Benzyl ⁸	$C_{14}H_7O_2.SC_7H_7$	242	9.71	8.87	Golden-yellow			
1,5-Dibenzyl	$C_{14}H_6O_2(SC_7H_7)_2$	176	14.17	14.50	Dull orange			
1,8-Dibenzyl	$C_{14}H_6O_2(SC_7H_7)_2$	189	14.17	14.34	Orange-red			

Table V
Benzyl-Thio-ether-anthraquinone Sodium Sulfonates

	Wa	iter	Sodium	Dry basis
Formula	Calc.	Found %	Calc.	Found %
1,5-C ₇ H ₇ S.C ₁₄ H ₆ O ₂ .SO ₃ Na.2H ₂ O	7.69	6.95	5.32	5.24
1,8-C ₇ H ₇ S.C ₁₄ H ₆ O ₂ .SO ₃ Na.3H ₂ O	11.11	11.80	5.32	5.72

Table~VI Alkyl-benzyl-anthraquinone-dithio-ethers. $RS.C_{14}H_6O_2.SC_7H_7$

	M.	p.	Sulfur	Sulfur found			
	1,5-	1,8-	Calc.	1,5- %	1,8-	Color	
Alkyl, R	°C.	°C.	%	%	%	1,5-	1,8-
Methyl	276	262	17.03	17.31	16.96	Gold	Crimson
Ethyl	208	164	16.43	16.86	16.81	Orange	Orange
Propyl	210	181	15.86	16.02	16.04	Orange	Orange
Butyl	235	185	15.32	15.18	15.03	Orange-yellow	Orange-red
iso-Propyl	239	229	15.86	16.18	16.12	Orange	Orange-red
iso-Amyl	211	189	14.83	15.00	14.99	Orange	Orange-red

TABLE VII
BENZYL-ANTHRAQUINONE SULFONES

		Sulfu	r %
Formula	M.	p. Calc.	Found
rormula	, c.	· ~ %	%
1-Benzyl ⁹ C ₁₄ H ₇ O ₂ .SC ₇ H ₇	233	}	
1,8-Dibenzyl C ₁₄ H ₆ O ₂ (SC ₇ H ₇) ₂	202	2 12.42	12.30

Table VIII
ALKYL-BENZYL-ANTHRAQUINONE DISULFONES, RSO₂.C₁₄H₅O₂.SO₂C₇H₇

	1.5-M	p.	Sulfur Calc.	Sulfur	
Alkyl, R	°.C.	1,8- ° C.	%	1,5- %	1,8-
Methyl	280	255	14.56	14.68	14.48
Ethyl		242.5	14.11	13.98	14.22
Propyl	215	227	13.69	13.70	13.80
Butyl	228	210	13.29	13.41	13.20
iso-Propyl			13.69	13.85	
iso-Amyl	202	201	12.91	12.75	12.60

⁸ Prepared by Gattermann, who gave m. p. 240° [Ann., 393, 113 (1912)].

⁹ Prepared by Gattermann, who gives m. p. 231° (Ref. 8, p. 139).

Reactions with Iso-Propyl Mercaptan

Preparation of iso-Propyl Mercaptan.—The mercaptan was prepared in the same way as benzyl mercaptan, using iso-propyl bromide as described by Claus. ¹⁰ The reaction mixture, in this case, after 4 days was distilled on the water-bath. The distillate was diluted with water, the mercaptan separated, dried over calcium chloride and redistilled; yield, 60%.

Reactions with Anthraquinone Sodium Sulfonates.—The speed of reaction of this substance with anthraquinone sulfonic acids at 100° was naturally very low on account of the low boiling point, 57° . The mixtures were refluxed for 12 hours and the yields averaged above 40%. The properties of the derivatives formed are given in the tables below.

Table IX
Iso-Propyl-anthraquinone-thio-ethers

	Sullur					
	Formula	M. p. °C.	Calc.	Found %	Color	
1-isoPropyl	C14H7O2.SCH(CH3)2	134	11.36	11.37	Gold	
1,5-Di-isopropyl	C14H6O2[SCH(CH3)2]2 148	17.99	18.04	Orange	
1,8-Di-isopropyl	C ₁₄ H ₆ O ₂ [SCH(CH ₃) ₂	$]_2$ 181	17.99	18.33	Orange-red	

TABLE X

ISO-PROPYL-THIO-ETHER-ANTHRAQUINONE SODIUM SULFONATES

	Wat	er	Sodium	Dry basis
and the second s	Cale.	. Found	Calc.	Found
Formula	%	%	%	%
$1,5-(CH_3)_2CHS.C_{14}H_6O_2.SO_3Na.2H_2O$	8.57	7.80	5.98	5.70
1,8-(CH ₃) ₂ CHS.C ₁₄ H ₆ O ₂ .SO ₃ Na.3H ₂ O	12.33	11.64	5.98	5.78

TABLE XI

ALKYL ISO-PROPYL-ANTHRAQUINONE-DITHIO-ETHERS, RS.C14H6O2.SCH(CH3)2

	M.	. p.	Sulfur	Sulfur			
Alkyl, R	°C.	°C.	calc.	1,5- %	1,8- %	Color	1,8-
Methyl	184	189	19.53	19.58	19.63	orange	crimson
Ethyl	163	176	18.73	19.01	18.52	gold	crimson
Propyl	133	135	17.99	18.24	18.13	gold	orange-red
Butyl	114	131	17.31	17.40	17.71	orange-yellow	orange-red
iso-Amyl	97	109	16.68	16.24	16.78	brownish	orange-red

Oxidation of Iso-propyl-anthraquinone-thio-ether and dithio-ethers

On oxidation of α -iso-propyl-anthraquinone-thio-ether with fuming nitric acid, 81% was converted into α -anthraquinone sulfonic acid which was identified by conversion into butyl-anthraquinone-thio-ether; m. p. 114°. A small amount of the sulfone, (CH₃)₂CHSO₂.C₁₄H₇O₂, was obtained, m. p. 182°

Calc. for C₁₇H₂₁O₄S: S, 10.20. Found: 10.30.

Similarly, the 1,5 mixed dialkyl dithio-ethers containing *iso* propyl gave small yields of the disulfones, 80 to 85% being oxidized to the alkyl sulfone-sulfonic acids. The melting points and analyses of these disulfones are given in Table XII.

¹⁰ Claus, Ber., 5, 656 (1872).

From the corresponding 1,8-dithio-ethers no disulfones could be obtained. The 1,8-anthraquinone disulfonic acid resulting from the oxidation of the di-isopropyl-dithio-ether was titrated and required over 96% of the calculated amount of alkali.

The 1,5- and 1,8-alkyl sulfone-sulfonic acids obtained above were boiled with butyl mercaptan under the usual conditions and converted into the corresponding alkyl sulfone-butyl-thio-ethers, the melting points of which are given in Table XIII. All are yellow solids very slightly soluble in water. For identification they were oxidized to the dialkyl disulfones described in the previous article.

TABLE XII

1,5-Alkyl-isopropyl-anthraquinone			DISULFON	res, RSO_2 .	$RSO_2.C_{14}H_6O_2.SO_2CH(CH_3)_2$			
isoPropyl alkyl	Methyl	Ethy1	Propyl	Butyl	isoPropyl	isoAmyl		
M. p., ° C.	235	213	203	186	222	172		
Sulfur, calc., found	16.34, 16.60;	15.78, 16.00;	15, 25, 15, 31;	14.76, 14.92;	14.30, 14.20;	15.25, 15.38		

TABLE XIII

ALKYL SULFONE-BUTYL-THIO-ETHERS, RSO2.C14H6O2.SC4H9

Alkyl	Methyl	Ethyl	Propyl	Butyl	isoAmyl
M. p., 1,5-:1,8-, ° C.	256:162	210:140	204: 132	162: 126	189:121

Reactions with Monothio-ethylene Glycol

This mercaptan was prepared according to the methods of Rosen and Reid¹¹ and of Bennett.¹² When freshly prepared it reacted with the anthraquinone sulfonic acids under the same conditions as did butyl mercaptan with about the same yields, but poor results were obtained when the mercaptan was not fresh. The monothio-ether had been previously prepared by Gattermann by another method. He gives the same melting point. Owing to the presence of the hydroxyl group, these thio-ethers show a slight solubility in water. The data for the compounds prepared are found in Table XIV. The acetates were made by treating with acetyl chloride and were recrystallized from acetic acid, the hydroxy compounds from butyl alcohol.

Table XIV
Derivatives of Monothio-ethylene Glycol

			Sul	
Substituents	M. p.	Calc.	Found	Color
1-SCH ₂ CH ₂ OH	178			orange
1-SCH ₂ CH ₂ OCOCH ₃	146			yellow
1,5-(-SCH ₂ CH ₂ OH) ₂	224	17.79	17.37	orange
1,5-(-SCH ₂ CH ₂ OCOCH ₃) ₂	199	14.43	14.60	yellow
1,8-(-SCH ₂ CH ₂ OH) ₂	206	17.79	17.30	red
1,8-(-SCH ₂ CH ₂ OCOCH ₃) ₂	159	14.43	14.54	yellow

¹¹ Rosen and Reid, This Journal, 44, 634 (1922).

¹² Bennett, J. Chem. Soc., 120, 422 (1921).

Reactions with Ethylene Mercaptan

Preparation of Ethylene Mercaptan.—Ethylene mercaptan was made according to the method of Fasbender¹³ with the following modifications. The mixture of the alcohol-water solution of sodium hydrosulfide and of ethylene bromide was allowed to stand for 4 days in cold water, with frequent shaking. The mixture was diluted with water, the mercaptan layer filtered off, dried with calcium chloride and distilled under reduced pressure; yield, about 30%. The mercaptan is exceedingly unstable and gives on heating a large quantity of a white crystalline compound. It is the formation of this compound, containing a high percentage of sulfur that made a study of the reactions of ethylene mercaptan so difficult.

Reaction of Ethylene Mercaptan with Anthraquinone Sulfonic Acids.—Ethylene mercaptan was found to react quite readily with the mono- and disulfonates, giving yields of about 80% of yellow powders. In every case, however, these powders were impure, giving various analyses for sulfur and no definite melting points. One attempt at purification of the monosulfonate reaction product gave a substance that contained 21.75% of sulfur. It did not melt below 250° , showing the absence of appreciable sulfur-containing impurities which were found in most cases to lower the melting points of the crude products to below 100° . The analysis points to the possible compound, $C_{14}H_7O_2.SCH_2CH_2S.CH_2CH_2S.CH_4H_7O_2$ (sulfur: calc., 21.42%), an oxidation product of the derivative $C_{14}H_7O_2SCH_2CH_2SH$ first formed.

1,5-Butyl-anthraquinone-sulfone Sodium Sulfonate,

C4H9SO2.C14H6O2.SO3Na, and its Reactions

The thio-ether sodium sulfonate, or "gold salt," is dissolved in about 2 parts by weight of fuming nitric acid and the solution evaporated to dryness on the water-bath. The oxidation to the sulfone-sulfonate is practically quantitative. This substance was dissolved in a minimum amount of hot water and the solution evaporated until crystals formed. These were separated and the solution was cooled. Nothing further separated until the temperature was below 30° . The crystals from hot water contained 2.89% of water and those from cold, 3.59%; calc.: 0.5 H₂O, 2.05%; 1 H₂O, 4.02%.

The sulfone sodium sulfonate is far more soluble and reacts with mercaptans far more rapidly than the thio-ether sodium sulfonate.

To a boiling solution of 2 g. of this salt in 50 cc. of water, with 4 equivalents of sodium hydroxide, butyl mercaptan was added in slight excess. The butyl-thio-etheranthraquinone-butyl-sulfone separated immediately. The boiling was continued for a few minutes and the crystals were separated and washed with hot water. The yield was practically quantitative.

Analysis. Calc. for C₄H₉S.C₁₄H₆O₂.SO₂C₄H₉: S, 15.40. Found: 15.37.

Fuming nitric acid oxidized it to 1,5-dibutyl-anthraquinone-disulfone, m. p., 184.5°, as described by Reid, Mackall and Miller. Corresponding products were made from other mercaptans. Because of the volatility of methyl mercaptan the reactants were sealed in a tube which was then suspended in boiling water. The melting points of thioether-sulfones and the disulfones into which they were converted by oxidation are given in Table XV.

¹³ Fasbender, Ber., 20, 460 (1887).

TABLE XV

ALKYL THIO-ETHER-ANTHE	RAQUINON	ie-butyi	L-SULFON	es and	DISULFONES
Alkyl, R	Methyl	Ethyl	Propyl	Butyl	isoAmyl
RS.C14H6O2.SO2C4Hg, m. p., ° C.	228	214	201	162	152
SO CUHO SOCH m n ° C	264	104	220	184 3	5 203.5

This reaction, which takes place so quickly and with such high yields, offers an excellent means of identifying mercaptans. For some unknown reason, the melting points of the alkyl thio-ether-butyl-sulfones are not as sharp as is desirable but the disulfones into which they are readily oxidized are excellent derivatives for identification as they are readily purified and melt sharply.

Thiophenol reacts with the butyl-sulfone sodium sulfonate under the same conditions as the mercaptans, though the reaction is slower; yield, 80%. The compound was recrystallized from acetic acid and did not melt even at 350°.

Analysis. Calc. for C6H5S.C14H6O2.SO2C4Hg: S, 14.69. Found: 15.11.

The same reaction takes place with p-nitro-thiophenol though the product remains in solution in the excess of alkali from which it was precipitated by acidifying. The product was extremely insoluble and difficult to purify. It melted above 300° and contained 14.03% of sulfur; calc., 13.32%.

Several attempts were made to prepare the oxygen ether, $C_4H_9O.C_1_4H_9O.2.SO_2C_4H_9$, by using butyl alcohol instead of the mercaptan but no such compound could be obtained. Long boiling in alkaline solution does not give any appreciable amount of the hydroxy derivative.

Summary

The replacement of sulfonic acid groups in the anthraquinone-sulfonic acids has been further studied using benzyl, p-nitrobenzyl, and isopropyl mercaptans and mono- and dithio-ethylene glycols. All of these react, but the second and last do not give products that can be purified.

The *iso*propyl-thio-ethers can sometimes be oxidized to sulfones but usually go to the sulfonic acids.

When 1,5- butyl-thio-ethers-anthraquinone sodium sulfonate is oxidized, the corresponding butyl-sulfone sulfonate is obtained in quantitative yield. This reacts extremely rapidly with mercaptans to form 1,5-butyl-sulfone-anthraquinone alkyl thio-ethers. This reaction offers a ready method for the identification of mercaptans.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

THE CONSTITUTION OF THE DICHLOROHYDROXY-ETHYLIDENE-BIS-NITRO-ANILINES

By Alvin S. Wheeler and Samuel C. Smith¹ Received May 23, 1923

In an attempt to reduce the 3 isomeric Schiff's bases obtained by the condensation of chloral and the nitro-anilines Wheeler and Glenn² noted that treatment of these bases with alcoholic potash produced a brilliant red compound. The red compound, however, on purification became yellow and analysis showed that 1 chlorine atom had been replaced by an hydroxyl group, according to the equation: $CCl_3CH(NHC_6H_4NO_2)_2$ + $KOH = CCl_2OHCH(NHC_6H_4NO_2)_2$ + KCl. Sodium methylate gave a product containing the methoxy group in place of a chlorine atom and more recently Wheeler and Smith³ prepared the ethoxy derivative, improved the general method of preparation by using acetone as the solvent for the reaction mixture and extended the reaction to o-nitro-aniline. The group now included the hydroxy, methoxy and ethoxy derivatives of the o- and p-nitro-anilines. No derivatives were obtainable from the Schiff base obtained from m-nitro-aniline.

Having lately some doubt as to the correctness of our idea in attaching the hydroxyl group to the carbon atom to which 2 chlorine atoms are already joined, we undertook a special study to determine the location of the hydroxyl group as well as the methoxy and ethoxy groups. No compounds are known that contain the hydroxyl group and chlorine attached to the same carbon atom. Such compounds, if formed, usually break up with the elimination of hydrogen chloride. In the compounds under review it seemed likely that the hydroxyl group had wandered to the α -carbon atom, producing a tertiary alcoholic group, thus,

$$\begin{array}{c|c} & & & & & & & & & \\ CCl_2OH & & & & & & \\ O_2N & & & NH-CH-NH & & NO_2 & & & NHC(OH)NH & & NO_2. \end{array}$$

We can readily imagine that the hydroxyl group momentarily takes the place of 1 of the 3 chlorine atoms attached to the β -carbon atom and then wanders to the α -carbon atom in order to form the more stable compound. In order to determine the position of the hydroxyl group the compound was decomposed with alkali. p-Nitro-aniline was readily identified among the decomposition products but no other compound of significance could

¹ This paper constitutes Part I of a thesis submitted in June, 1923, to the Faculty of the University of North Carolina by Samuel C. Smith in candidacy for the degree of Doctor of Philosophy.

² Wheeler and Glenn, J. Elisha Mitchell Sci. Soc., 19, 63 (1903).

² Wheeler and Smith, This Journal, 41, 1862 (1919).

be isolated. Concd. sulfuric acid gave a very small quantity of a liquid of strange odor. This liquid was not investigated. Fruitful results however were obtained when the substance was treated with hot 30% sulfuric acid. The compound dissolved and when the solution cooled crystals were deposited which after purification melted at 127°. Neutralization of the mother liquor with sodium hydroxide caused the precipitation of p-nitro-aniline, melting at 147°. The course of the reaction appeared to be: $O_2NC_6H_4NHC(OH)(CCl_2H)NHC_6H_4NO_2 \longrightarrow H_2SO_4$ \longrightarrow O₂NC₆H₄NHCOCCl₂H(p) + O₂NC₆H₄NH₂(p). The first product should be p-nitrodichloro-acetanilide. We could find no such anilide described in the literature, dichloro-acetanilide being the nearest to it. The preparation of the latter compound from dichloro-acetic acid and aniline requires the presence of phosphorus pentoxide.4 Using this method with dichloro-acetic acid and p-nitro-aniline we obtained p-nitrodichloroacetanilide which proved to be identical in physical and chemical properties with the decomposition product described above.

In view of the fact that this bis-nitro-aniline, as well as all of the others, splits easily, cleanly and quickly with dil. acid, giving in every case a product containing oxygen attached to the α -carbon atom, it seems clear that in these derivatives of Schiff's bases the hydroxyl and alkoxy groups are attached to the carbon atom which is joined to the nitrogen atoms. Since the acid decomposition of the alkoxy derivatives yields p-nitro-aniline (or ortho) and not the alkylated nitro-anilines, the reaction must be written: 5 CCl₂HCOCH₃(NHC₆H₄NO₂)₂ + H₂SO₄ = CCl₂HCONH-C₆H₄NO₂ + NH₂C₆H₄NO₂ + CH₃HSO₄.

Experimental Part

p-Nitrodichloro-acetanilide, CCl2HCONHC6H4NO2

(a) By Acid Decomposition of Dichlorohydroxy-ethylidene-bis-p-nitro-aniline.—Ten g. of the hydroxyethylidene compound (m. p., 178°) was dissolved in 40 cc. of the 30% sulfuric acid and then heated for 2 minutes with a direct flame. The solution was then diluted with an equal volume of water and allowed to cool thoroughly. A heavy deposition of crystals of the anilide occurred. These melted at 124° and weighed 80% of the calculated amount. Recrystallization was best effected with 50% alcohol, 80% of the crude product being recovered in a pure condition. This new acetanilide forms pale yellow needles; m. p., 127°; CCl₂HCOH(NHC₆H₄NO₂)₂ + H₂SO₄ = CCl₂HCONHC₆H₄NO₂ + NO₂C₆H₄NH₂.H₂SO₄. p-Nitrodichloro-acetanilide is unstable toward alkalies but very stable in the presence of acids. It may be dissolved in acids, including nitric, and is unchanged on reprecipitation. It is insoluble in water and soluble in acetone, alcohol, benzene and chloroform.

⁴ Cech, Ber., 10, 1265 (1877).

⁵ If phosphorous pentoxide is omitted in the reaction between dichloro-acetic acid and o-toluidine, the product contains 3 chlorine atoms and, therefore, is not dichloro-o-toluidide. This surprising result led to a study of the reaction between dichloro-acetic acid and a number of aromatic amines. Part II of Mr. Smith's thesis will deal with this unusual reaction. It will be published shortly. A. S. W.

Analysis. Subs., 0.3167: AgCl, 0.3694. Calc. for $C_8H_5O_3N_2Cl_2$ (mol. wt., 249) Cl, 28.51. Found: 28.85.

p-Nitro-aniline, the second product of the reaction, was readily isolated from the mother liquor by the addition of an excess of alkali, as yellow needles; m. p., 147°.

(b) By Acid Decomposition of Dichloromethoxy-ethylidene-bis-p-nitro-aniline.— The methoxy derivative (m. p., 177°) was treated in the same manner with hot 30% sulfuric acid. The insoluble product, after recrystallization from 50% alcohol, melted at 127° and consisted of yellow needles.

Analysis. Subs., 0.2556: AgCl, 0.2941. Calc. for $\dot{C}_8H_6O_5N_2Cl_2$ (mol. wt., 249): C1, 28.51. Found: 28.46.

 $CCl_2HCOCH_3(NHC_6H_4NO_2)_2 + H_2SO_4 = CCl_2HCONHC_6H_4NO_2 + NO_2C_6H_4NH_2 + C-H_3HSO_4$,

(c) By Acid Decomposition of Dichloro-ethoxy-ethylidene-bis-p-nitro-aniline.— The ethoxy derivative (m. p., 147°) was treated with sulfuric acid in the same manner and the same product, melting at 127°, was obtained.

Analysis. Subs., 0.2542: AgCI, 0.2919. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl, 28.51. Found: 28.41.

(d) By the Action of Dichloro-acetic Acid on p-Nitro-aniline.—To 5.0 g. of p-nitro-aniline was added 5.0 g. of phosphorus pentoxide and 5.0 g. of dichloro-acetic acid. The mixture was heated under a reflux condenser for 10 minutes. Cold water was added and the whole was well shaken. The crystalline product was separated and recrystallized from 50% alcohol as light yellow needles; m. p., 127°.

Analysis. Subs., 0.1422: AgCl, 0.1632. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl, 28.51. Found: 28.34.

o-Nitrodichloro-acetanilide, CCl2HCONHC6H4NO2

(a) By Acid Decomposition of Dichlorohydroxy-ethylidene-bis-o-nitro-aniline.—Five g. of the hydroxy derivative (m. p., 143°) was dissolved in 20 cc. of hot 30% sulfuric acid and heated for 2 minutes. An equal volume of water was added; as the solution cooled a liquid separated. When this was removed from the acid solution and washed well, it solidified. When an attempt was made to recrystallize it from alcohol, it separated again as an oil. However, it was obtained in crystallized condition by solution in alcohol, 70% strength, at 70° and cooling, as bright yellow plates; m. p., 70–72°.

Analysis. Subs., 0.0748: AgCl, 0.0866. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl. 28.51. Found: 28.64.

The compound is insoluble in water but soluble in acetone, alcohol, ether, benzene and chloroform. The yield was 70%. The ortho compound was also obtained by the action of hot sulfuric acid on the methoxy and ethoxy derivatives of o-nitro-aniline. In each case the product melted at $70-72^{\circ}$ and crystallized in bright yellow plates.

(b) By the Action of Dichloro-acetic Acid on σ-Nitro-aniline.—Five g. of σ-nitro-aniline was mixed with 5.0 g. of phosphorus pentoxide and 5.0 g. of dichloro-acetic acid. Much heat was generated. The mixture was heated for a few minutes longer, and then poured into 200 cc. of cold water, whereupon a heavy oil separated, which, after it had stood overnight, solidified; yield, 6 g. It forms yellow plates; m. p., 70–72°.

m-Nitrodichloro-acetanilide, CCl2HCONHC6H4NO2

Since trichloro-ethylidene-bis-m-nitro-aniline gives no hydroxy or alkoxy derivatives with basic reagents we could only use the direct method for preparing the meta compound. Equal amounts of m-nitro-aniline, phosphorus pentoxide and dichloro-acetic

⁶ Ref. 3, p. 1864.

acid were heated together. The product separated as an oil when the mixture was poured into water, but it solidified after standing a day. The crude product was light brown and melted at 65°. Purification by alcohol raised the melting point to 103°. It crystallizes in almost colorless needles, that are soluble in acetone, alcohol, ether, benzene or chloroform.

Analysis. Subs., 0.1591: AgCl, 0.1849. Calc. for $C_8H_6O_3N_2Cl_2$ (mol. wt., 249): Cl, 28.51. Found: 28.75.

Summary

- 1. The three new nitrodichloro-acetanilides were prepared.
- 2. The p-compound appeared as a decomposition product when dichlorohydroxy-ethylidene-bis-p-nitro-aniline was treated with hot dil. sulfuric acid. Its production established the location of the hydroxyl group on the α -carbon. The methoxy and ethoxy derivatives gave the same anilide.
 - 3. The o-nitrodichloro-acetanilide was similarly obtained.
- 4. The *ortho* and *para* compounds were also obtained by the action of dichloro-acetic acid on the nitro-anilines in the presence of phosphorus pentoxide.
- 5. The *meta* isomer could be obtained only by the direct method since the hydroxy and alkoxy derivatives of trichloro-ethylidene-bis-*m*-nitro-aniline cannot be prepared

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

MERCURATED 1-METHYL-1,2-DIHYDRO-BENZOFURANS

By Lindley E. Mills with Roger Adams¹ Received May 24, 1923

In a recent paper by Roger Adams, F. L. Roman and W. N. Sperry,² involving a discussion of the structure of compounds produced from olefins and mercury salts, it was shown that mercury salts and *o*-allylphenol reacted readily to give mercurated 1-methyl-1,2-dihydro-benzofurans according to the following equation.

$$\begin{array}{c}
\text{OH} \\
\text{CH}_2\text{CH} = \text{CH}_2
\end{array}
\rightarrow
\begin{array}{c}
\text{OH} \\
\text{CH}_2\text{CH} \times \text{CH}_2\text{HgX}
\end{array}
\rightarrow
\begin{array}{c}
\text{CHCH}_2\text{HgX} + \text{HX}
\end{array}$$

A study of the preparation of the corresponding compounds from mercury salts and substituted o-allylphenols, and a study of their chemical reactions had been made. In view of the fact that the mercurated 1-methyl-1,2-dihydro-benzofurans, in contrast to the compounds from mercuric salts

¹ This communication is an abstract of a thesis submitted by L. E. Mills in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Adams, Roman and Sperry, This Journal, 44, 1781 (1922).

and other olefins, are unusually stable toward hydrochloric acid, a comparison of the chemical reactions of these compounds with the chemical reactions of the alkyl mercuric halides and with the chemical reactions of the compounds from simple olefins and mercuric salts was of especial interest.

It has been shown that the addition of mercuric salts to *o*-allylphenols is a general one. Mercuric acetate and mercuric chloride react readily with the following compounds: 2-allyl-4-methylphenol, 2-allyl-5-methylphenol, 2-allyl-6-methylphenol, 2-allyl-4-bromophenol, 2-allyl-4-carboxyphenol, 2-allyl-6-carboxyphenol, 2-allyl-6-carboxyphenol and 2-allyl-4-carboxyvinylene-phenol. The only difference noticed among any of the reactions is the speed with which they take place. The yields are almost quantitative in every reaction.

The acetoxy or chloromercurimethyl-1,2-dihydro-benzofurans show the usual reactions of various types of acetoxy and chloromercuri compounds with solutions of bromides or iodides, giving the corresponding bromoor iodomercuri compounds. No mercuri-bis compounds or compounds free from mercury are formed by the action of iodides.³

The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with the greatest ease with both alcoholic potassium cyanide and alcoholic potassium thiocyanate to yield the corresponding cyanomercuri or thiocyanatemercuri compounds. It is impossible by longer refluxing with excess of reagent to convert these into the corresponding mercury-bis compounds.

$$\begin{array}{c} O \\ CHCH_2HgCl + MX \longrightarrow \begin{array}{c} O \\ CHCH_2HgX + MCl \\ CH_2 \end{array} \\ \text{where X = Br, I, SCN, CN.} \end{array}$$

This behavior of the 1,2-dihydro-benzofurans is in contrast to that of alkyl mercuric halides which generally give mercury-bis compounds, and to that of the compounds obtained from mercuric salts and olefins which lose their mercury entirely under such treatment, giving the original unsaturated compound.⁴ It is interesting to note that 2,5-dinitratemercurimethyl-dioxane

with the mercurated dihydro-benzofurans under consideration not only is stable to acid but also yields a dicyanomercuri compound by the action of aqueous potassium cyanide.⁵

- ³ Steinkopf and Bauermeister, Ann., 403, 57 (1914). Biilmann, Ber., 43, 574 (1910).
- 4 Hoffman and Sand, Ber., 33, 1344 (1900).
- ⁵ Sand, (a) *ibid.*, 33, 2679 (1900); 34, (b) 1387, (c) 1394 (1901).

The 1-hydroxymethyl-1,2-dihydro-benzofurans are readily obtainable from the corresponding chlorides by the action of absolute alcoholic sodium hydroxide. The sodium chloride is filtered and the alcoholic filtrate is concentrated to obtain the hydroxymercuri compounds. These substances are crystalline solids and have the expected property of being readily neutralized by all types of organic or inorganic acids such as hydrochloric, sulfuric, tartaric, oxalic, p-nitrobenzoic acids, etc. The hydroxymercuri compounds precipitate insoluble metallic hydroxides such as cupric hydroxide from neutral solutions of their salts.

Most aliphatic hydroxymercuri compounds recorded in the literature have been obtained from the corresponding bromides or iodides by the action of moist silver oxide. The present experiments suggest a better method for making these compounds. The mercury dialkyls made by the method of Marvel⁶ and others, when treated with mercuric chloride in alcohol, give quantitative yields of alkyl mercuric chlorides. When these are treated with sodium hydroxide in absolute alcohol, the corresponding hydroxides should be formed. This method has been tested in the case of methyl mercuric chloride with perfect success. Presumably, any of the series could be formed similarly.

The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with an alkaline solution of sodium stannite to give an immediate precipitate of metallic mercury and a quantitative yield of the corresponding allylphenol. No indication of an intermediate mercury compound was noted. The reaction of alkaline sodium stannite with both alkyl mercury salts and compounds of mercuric salts and olefines is usually to give compounds of the mercuri-bis type and metallic mercury. No previous example could be found in the literature in which mercury is completely removed from an organic mercury compound by means of sodium stannite.

The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react instantaneously with ammonium sulfide, potassium hydrosulfide or hydrogen sulfide in dil. acid solution to give quantitative yields of the corresponding allylphenol and mercuric sulfide. No intermediate organic mercuri sulfides were isolated. This reaction is in contrast to the action of sulfides upon alkyl mercuric salts which almost invariably form organic mercuri sulfides of varying stability; these decompose to mercury-bis compounds and mercuric sulfide. The su fide reagents react in different ways with compounds from olefins and mercuric salts; a complex organic mercuri sulfide may be formed, the mercuri grouping may be replaced by hydrogen, or the original unsaturated compound may be regenerated, this latter

⁶ Marvel and Gould, This Journal, 44, 153 (1922). Marvel and Calvery, ibid., 45, 820 (1923).

⁷ Dimroth, Chem. Zentr., 1901, I, 451. Ref. 5c.

reaction being analogous to that observed with the 1-halogen-mercuri-methyl-1,2-dihydro-benzofurans.8

Sodium thiosulfate is a reagent that has been used frequently for converting aromatic organic mercuric salts to the corresponding mercury-bis compounds. Very frequently an intermediate sodium thiosulfate-mercuri compound of the general formula RHgSSO₂Na has been isolated. Nothing could be found in the literature, however, on the action of sodium thiosulfate upon alkyl mercuric halides or upon compounds from olefins and mercuric salts. By treating 1-chloromercurimethyl-1,2-dihydro-benzofurans with a cold saturated solution of sodium thiosulfate, a 1-sodium thiosulfate-mercurimethyl-1,2-dihydro-benzofuran is obtained. The product darkens in the air in a few minutes and decomposition is complete within a few hours; when the substance is heated the decomposition is made much more rapid. Red mercuric sulfide and the corresponding allylphenol are formed. The compounds in general are so unstable that even recrystallization from water is impossible without decomposition.

The only reagent tested which converts the 1-halogen-mercurimethyl-1,2-dihydro-benzofurans into the corresponding mercury-bis compounds is sodium amalgam and alcohol. In the preliminary paper it was mentioned that 1-chloromercurimethyl-1,2-dihydro-benzofuran was converted readily to the corresponding mercury-bis compound in this way. It has now been found that other derivatives, such as the 1-chloromercurimethyl-4-methyl-1,2-dihydro-benzofuran, react in a similar manner under the same conditions. Sodium amalgam-alcohol also converts alkyl mercuric halides into mercury-bis compounds.

The mercurated 1-methyl-1,2-dihydro-benzofurans are unaffected by boiling with methyl iodide or acetyl chloride. Alkyl halides do not react with these reagents, but compounds from olefins and mercuric salts react with alkyl halides to regenerate the original olefin and with acetyl chloride to yield the acetyl derivative of the hydroxyl group without affecting the substituted mercury radical.⁹

The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with 2 atoms of bromine in cold chloroform suspension to yield a precipitate of mercuric salts and a solution containing 1-bromomethyl-1,2-dihydro-benzofuran. Under these conditions no hydrogen bromide is evolved, although when the proper precautions as regards temperature are not followed, hydrogen bromide is evolved and probably bromination in the benzene ring takes place.

It is obvious from the comparative reactions that have been made that

⁸ Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., 1921, pp. 50-53.

⁹ Ref. 4, p. 1349. Ref. 5b, p. 1393. Kutscheroff, Ber., 17, 21 (1884).

the mercurated-methyl-1,2-dihydro-benzofurans resemble in many of their reactions the alkyl mercuric halides, and in many others the compounds from olefins and mercuric salts. In some of the reactions such as those with potassium thiocyanate, potassium cyanide, sodium thiosulfate and sodium stannite, they may be said to stand midway between the two classes.

The reactions of these mercurated-1-methyl-1,2-dihydro-benzofurans, as described above, certainly offer still further convincing evidence that the compounds are not "molecular" substances but actually true addition compounds as suggested and discussed in the preliminary paper.

Experimental Part

The o-allylphenols used in this investigation were prepared according to the directions of Claisen.¹⁰ The 2-allyl-4-carboxyvinylene-phenol was prepared according to the same general procedure, and the details are given in the latter part of the experimental section.

The method of analysis for mercury in the various compounds was similar to that described in the preliminary article. A few minor details were changed; silver nitrate was standardized against very pure mercuric chloride in the same way as it was titrated in the analyses for mercury in the organic compounds. The mercuric chloride had been resublimed several times and was analyzed gravimetrically. Another slight change was that the solution containing the precipitate of mercuric sulfide was heated almost to boiling and hydrogen sulfide passed in again for a few minutes just before filtration.

General Method for the Preparation of Substituted 1-Mercurimethyl-1,2-dihydro-benzofurans.—To a solution of 1 molecular equivalent of mercuric acetate or mercuric chloride in water, 10 g. of a substituted oallylphenol was added slowly while the mixture was vigorously stirred. With the mercuric chloride a saturated solution was used, with the acetate about 10 g. of salt in each 100 cc. of water. When mercuric acetate was used, the time of addition was from 1/2 to 1 hour and stirring was continued for several hours longer to insure completion of the reaction. When mercuric chloride was used the substituted o-allylphenol was added slowly and a flocculent precipitate of product was formed. In the case of oallylphenol itself a rate of 4 to 5 drops per minute was found to give the best results. In the case of the substituted o-allylphenols it was found more convenient to add the phenol during a period of 1 hour and then to continue the stirring until the heavy oil solidified. Stirring was then discontinued and the solid material pulverized with a stirring rod and the mixture stirred again. Six to 8 hours was usually required for the complete procedure when 2-allyl-4-methylphenol, 2-allyl-5-methylphenol or

¹⁰ Claisen and Eisleb, Ann., 401, 21 (1913).

2-allyl-6-methylphenol was used, as compared to 3 hours for 2-allylphenol itself. The 2-allyl-4-bromophenol required 10 hours. The 2-allyl-6-carbomethoxyphenol required 15 hours' stirring and 2 days' standing. In the case of 2-allyl-4-carboxyphenol, 2-allyl-6-carboxyphenol and 2-allyl-6-carboxyvinylene-phenol the best results were obtained by adding just enough sodium hydroxide to a suspension of the carboxyphenol in water to dissolve it and then adding an aqueous solution to the theoretical amount of mercuric chloride. In each case a precipitate of the desired product began to form immediately and was complete in a few minutes.

With the exception of mercuric acetate with 2-allyl-5-methylphenol, 2-allyl-4-methylphenol and with 2-allyl-4-bromophenol, all of the compounds obtained were solids. The three just mentioned were obtained as oils and did not solidify under the conditions used. Their conversion, however, by treatment with sodium halide into the corresponding halogen mercury compounds, indicated without question that an addition had taken place.

The solid compounds were white and well crystallized. They were purified from alcohol, except 1-chloromercurimethyl-6-carbomethoxy-1,2-dihydro-benzofuran, for which methyl alcohol was used.

The 1-chloromercurimethyl-6-methyl-, 1-chloromercurimethyl-5-methyl-, 1-chloromercurimethyl-4-methyl-, and the 1-chloromercurimethyl-4-bromo-

Table I

Mercurated 1,2-Dihydro-benzofurans Prepared by the Addition of Mercury

Salts to Substituted Ortho-allylphenols

				F	Ig
1.0 Dillord or homoforms	M. p.	Subs. G.	AgNO ₃	Calc.	Found
1,2-Dihydro-benzofurans				%	%
1-acetoxymercurimethyl-6-methyl	113	0.1257	11.80	49.36	49.57
		.1428	13.28		49.11
			N. F. a - 0.0263		
1-chloromercurimethyl-6-methyl	91	.2168	21.38	52.35	52.06
			N. F. -0.0263		
1-acetoxymercurimethyl-5-methyl	oil				
1-chloromercurimethyl-5-methyl	127.5	.1825	18.04	52.35	52.18
			N. F0.0263		
1-acetoxymercurimethyl-4-methyl	oil				
1-chloromercurimethyl-4-methyl	99.5	.4508	44.90	52.35	51.92
			N. F. -0.0566		
1-acetoxymercurimethyl-4-bromo	oil				
1-chloromercurimethyl-4-bromo	108	.6575	25.73	44.77	44.22
		.5697	22.30		44.23
			N. F. -0.0566		
1-chloromercurimethyl-6-carboxy	200 with de-	.2525	10.85	48,55	48.55
	comp.		N. F. -0.0566		
1-chloromercurimethyl-6-carbomethoxy	107 with de-	.1721	15.22	46.95	46.70
医乳头 机拉克斯特 医多克氏 医多克氏管	comp.	.1018	8.98		46.61
			N. F. -0.0263		
1-chloromercurimethyl-4-carboxy	212-213 with	.2089	19.45	48.55	48.43
	decomp.		N. F0.0566		
1-chloromercurimethyl-4-carboxyvinylene	300 with de-	.1429	12.42	45.68	45.21
	comp.		N. F0.0263		

^a N. F. = normality factor.

1,2-dihydro-benzofurans described in the following table were made not only by addition of mercuric chloride to the proper o-allylphenol, but also by the treatment of the corresponding acetate with sodium chloride solution according to the general method described immediately after Table I.

General Method for the Conversion of 1-Chloromercuri- or 1-Acetoxy-mercuri-methyl-1,2-dihydro-benzofurans into the Corresponding Bromides and Iodides.—A solution of 5 g. of the chloromercuri- or acetoxy-mercurimethyl-1,2-dihydro-benzofuran in absolute alcohol was mixed with a boiling, absolute alcohol solution of 1 molecular equivalent of potassium halide. As the mixture cooled the halogen mercury compound separated. After this was washed with water to remove the potassium salts, it was necessary to make one recrystallization from alcohol in order to obtain a pure product.

The conversion of the acetoxymercuri compounds to the corresponding chlorides, bromides or iodides, took place more readily than the conversion of the chloromercuri compounds to bromides or iodides. It was often unnecessary to heat the reaction mixture in order to effect the former conversions.

The same reaction could be carried out by dissolving or suspending 5 g. of the acetoxy or chloromercuri compounds in 200 cc. of water and then heating the mixture for about an hour on a water-bath with an aqueous solution of 1 molecular equivalent of potassium halide. As the reaction mixture cooled the precipitate solidified; it was separated, washed and recrystallized from alcohol.

Table II
Mercurated 1,2-Dihydro-benzofurans

	,			H	9
1,2-Dihydro-benzofurans	М. р. °С.	Subs. G.	AgNO ₃ Cc.	Calc.	Found %
1-iodomercurimethyl-6-methyl	88	0.1529	12.19	42.35	42.10
		.2016	16.00		41.92
			N. F. -0.0263		
1-iodomercurimethyl-5-methyl	131.5	.1840	15.00	42.35	42.41
			N. F. -0.0263		
1-iodomercurimethyl-4-methyl	94	.2112	16.82	42.35	42.06
		.1687	13.36		41.83
			N. F. -0.0263		
1-bromomercurimethyl-4-bromo	93	.6536	23.25	40.73	40.18
바다를 보고 하는데 눈으로 보고 있다면?		.4870	17.45		39.57
그래마 아들 그는 말로 하는데 하는데 하다.			N. F. -0.0566		
1-iodomercurimethyl-4-bromo	101	.4968	16.27	37.18	37.00
교통, 프로그램 - 최근 기반 시대 - 시간 시간이		.4853	15.86		36.92
			N. F. -0.0566		

1-Hydroxymercurimethyl-1,2-dihydro-benzofurans.—From a solution of 10 g. of the substituted 1-chloromercurimethyl-1,2-dihydro-benzofuran in 1 molecular equivalent of sodium hydroxide in 50 cc. of warm absolute

ethyl alcohol, sodium chloride immediately precipitated. The solution was filtered and evaporated to half its volume and then cooled slowly. It was finally allowed to remain in an ice-salt mixture for several hours, and the sides of the beaker were rubbed vigorously from time to time with a glass rod. Crystallization gradually took place and the crystals were separated, washed with a small amount of cold alcohol and dried. They were then recrystallized in the same manner from 95% alcohol.

The hydroxymercuri compounds were readily soluble in most organic solvents but only slightly soluble in water, giving solutions which were slightly alkaline to litmus.

All the hydroxymercuri compounds studied were very readily soluble in alcohol, tended to form supersaturated solutions and then to precipitate as oils. By following the procedure indicated above, white crystalline solids were obtained except in the case of 1-hydroxymercurimethyl-6-methyl-1,2-dihydro-benzofuran, which was obtained only as an oil. The yields of the hydroxymercuri compounds were quantitative.

1-Hydroxymercurimethyl-1,2-dihydro-benzofuran was also obtained in 80% yield by refluxing 5 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran with the calculated amount of moist, freshly precipitated silver oxide in 75 cc. of ethyl alcohol.

Table III 1-Hydroxymercurimethyl,-1,2-dihydro-benzofurans

			H		
М. р. °С.	Subs. G.	AgNO ₃ Cc.	Calc.	Found %	
152	0.1162	11.86 N. F0.0280	57.19	57.34	
thick oil	.1462	14.33 N. F0.0280	55.00	55.07	
149	.2749	27.00 N F -0.0280	55.00	55.18	
	152 thick oil	° C. G. 152 0.1162 thick .1462 oil	$\begin{array}{cccc} 152 & 0.1162 & 11.86 \\ & & \text{N. F.} -0.0280 \\ \text{thick} & .1462 & 14.33 \\ \text{oil} & & \text{N. F.} -0.0280 \\ \end{array}$	152 0.1162 11.86 57.19 N. F0.0280 thick .1462 14.33 55.00 oil N. F0.0280 149 .2749 27.00 55.00	

Mercurated 1,2-Dihydro-benzofurans by Neutralization of the Hydroxymercuri Derivatives with Acids.—When alcoholic or aqueous solutions of 1-hydroxymercurimethyl-1,2-dihydro-benzofurans were neutralized with dil. hydrochloric acid, the corresponding chloromercuri compounds were precipitated. For the preparation of the organic acid salts the hydroxymercuri compounds were dissolved in hot alcohol and the solution was then diluted with hot water, the amount added being insufficient to cause the precipitation of any of the mercury compound. A hot alcoholic or aqueous alcoholic solution of the proper acid was then added until a faint acid reaction to litmus was obtained. The solution was allowed to cool and was filtered. The precipitated products were recrystallized from alcohol in which they were somewhat soluble when hot and practically insoluble when cold. All of the salts were well-crystallized solids.

The p-nitrobenzoates of the mercury compounds were yellow but all the others were white.

Table IV
Mercurated 1,2-Dihydro-benzofurans

•				F	[g
1,2-Dihydro-benzofurans	М. р. °С.	Subs. G.	AgNO3 Cc.	Calc.	Found
1-tartrate-di(mercurimethyl	192 with decomp.	0.3165	27.86 N. F0.0280	49.20	49.45
1-oxalate-di(mercurimethyl	175	.2069	19.51 N. F0.0280	53.11	52.98
1-(p)nitrobenzoate-mercurimethyl	148	.2606	18.61 N. F0.0280	40.14	40.12
1-(p)nitrobenzoate-mercurimethyl-6-methyl	162.5	.2943	20.53 N. F0.0280	39.04	39.19
1-(p)uitrobenzoate-mercurimethyl-4-methyl	136.5	.2386	16.50 N. F0.0280	39.04	38.85

1-Cyanomercurimethyl and 1-Thiocyanate-mercurimethyl Derivatives of Substituted 1,2-Dihydro-benzofurans.—Into a hot saturated solution of 1 molecular equivalent of potassium cyanide or potassium thiocyanate in absolute alcohol, was stirred 10 g. of powdered 1-chloromercurimethyl-1,2-dihydro-benzofuran. An immediate precipitation of potassium chloride occurred. After a few minutes the mixture was filtered and the filtrate allowed to cool. The cyanomercuri or thiocyanatemercuri compound crystallized. Upon filtering and concentrating the filtrate, or upon pouring it into water a further quantity of the material was obtained. These substances are readily purified from alcohol, forming white crystals. The yield in every case was almost quantitative.

Table V
Mercurated 1,2-Dihydro-benzofurans

			H	g
1,2-Dihydro-benzolurans	M. p. Subs. ° C. G.	AgNO₃ Cc.	Calc.	Found
1-thiocyanatemercurimethyl	112.5 0.2028	18.40	51.21	50.97
		N. F. -0.0280		
1-cyanomercurimethyl	162 .1723	17.03	55.76	55.53
		N. F. -0.0280		
1-thiocyanatemercurimethyl-4-methyl-	102.5 .2761	24.34	49.43	49.53
		N. F. -0.0280		
1-cyanomercurimethyl-4-methyl	148 .3050	29.02	-53.67	53.45
		N. F. -0.0280		11 11

1-Sodiumthiosulfate-mercurimethyl-1,2-dihydro-benzofuran.—Just enough water was added to 10 g. of finely ground 1-chloromercurimethyl-1,2-dihydro-benzofuran to moisten it, and the latter was then quickly and thoroughly stirred into a hot saturated solution of 3.4 g. of sodium thiosulfate in water. A large amount of the material turned black because of the formation of mercuric sulfide. The mixture was immediately filtered hot by gentle suction and the filtrate cooled. Glistening white scales of the sodium salt separated. These were separated and dried on a porous plate.

Analysis. Subs., 0.2184: 18.61 cc. of 0.02608 N AgNO₃. Calc. for C₃H₉HgO₄S₂-Na: Hg, 44.90. Found: 44.75.

This compound was also prepared by triturating together the same quantities of materials in the cold for a few minutes and then filtering and washing with a very small amount of cold water. The product weighed 11 g., which is about a 92% yield. No method for recrystallization was found.

It is very soluble in hot water, decomposing into mercuric sulfide and o-allylphenol. After the original reaction mixture had been warmed on the steam-bath for 2 hours the decomposition of the intermediate sodium salt was complete. The sulfide was filtered and washed well with acetone. The mixture of the washings and the filtrate was extracted with ether and dried with calcium chloride. A yield of 2.9 g. of o-allylphenol, or 87%, was obtained from 10 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran.

When heated, the salt turned dark at about 120°. At ordinary temperatures the decomposition proceeded more slowly. The crystals began to darken after a few minutes and were completely decomposed after about 12 hours. All the experiments in which the decomposition took place at room temperature gave rise to the red modification of mercuric sulfide.

1-Sodiumthiosulfate-mercurimethyl-4-methyl-1,2-dihydro-benzofuran.—This substance was prepared in the same way as was the preceding compound which it resembled closely in properties. The yield by the hot method was low, by the cold method almost quantitative. The properties of the product were identical with those of the previous compound.

Analysis. Subs., 0.2491: 20.52 cc. of 0.02618 N AgNO₃. Calc. for $C_{10}H_{11}HgO_4$ -S₂Na: Hg, 43.53. Found: 43.25.

When the reaction mixture was warmed for 2 hours and the 2-allyl-4-methylphenol recovered as in the previous case of o-allylphenol, an 85% yield was obtained.

Reaction of 1-Chloromercurimethyl-1,2-dihydro-benzofurans with Alkaline Sodium Stannite Solution.—An alkaline solution of sodium stannite was prepared by dissolving 3 g. of stannous chloride crystals in 50 cc. of water and then adding 50% more of 10% sodium hydroxide solution than was sufficient just to dissolve the precipitate. A thin paste of 5 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran and water was then slowly stirred in. A gray precipitate of mercury was formed immediately. After the liquid had been warmed on the steam-bath for a few minutes it was decanted, made acid with dil. hydrochloric acid and extracted with ether. The ether solution was dried over calcium chloride and the ether distilled. There was obtained 1.4 g. or an 83% yield of o-allylphenol.

A yield of 85% of 2-allyl-4-methylphenol was obtained from 5 g. of 1-chloromercurimethyl-4-methyl-1,2-dihydro-benzofuran by the same procedure.

Reaction of 1-Chloromercurimethyl-1,2-dihydro-benzofurans with Sulfides. WITH HYDROGEN SULFIDE.—A suspension of 5 g. of finely ground 1-chloromercurimethyl-1,2-dihydro-benzofuran was made in 100 cc. of water containing 2 cc. of coned. hydrochloric acid and the solution shaken frequently while being saturated with hydrogen sulfide. The precipitate of mercuric sulfide was allowed to settle and the liquid decanted. The mercuric sulfide was washed thrice with acetone by decantation and the washings were added to the liquid first decanted. After extraction with ether there was obtained 1.3 g. or a 77% yield of o-allylphenol. Similar treatment of 1-chloromercurimethyl-4-methyl-1,2-dihydro-benzofuran gave an 85% yield of 2-allyl-4-methylphenol.

With Ammonium Sulfide.—Ten g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran was suspended in 100 cc. of water containing 5 cc. of concd. ammonium hydroxide (d., 0.90) and saturated for 1 hour with hydrogen sulfide while it was shaken frequently. The mercuric sulfide was separated and the o-allylphenol recovered as in the preceding case; yield, 3.2 g., or 90%. A similar result was obtained with the 4-methyl derivative.

WITH POTASSIUM HYDROSULFIDE.—To 5 g. of 1-chloromercurimethyl-1,2-dihydro-

benzofuran suspended in 100 cc. of water was added slowly with stirring a solution containing 2 g. of potassium hydrosulfide in 50 cc. of water. The precipitated mercuric sulfide was filtered and the o-allylphenol recovered as in the preceding case. The yield was 1.5 g., or 89%. This reaction was also carried out in absolute alcohol with similar results.

In no case was any intermediate organic mercuric sulfide isolated. The initial precipitate in each instance was black. It was noted that upon first forming, the precipitate was somewhat bulky and flocculent, indicating the possible formation of a very unstable organic mercuri sulfide. This precipitate became granular after it had stood for a few minutes.

1,1-Mercuridimethylenebis-(4-methyl-1,2-dihydro-benzofuran).—A mixture of 15 g. of 1-chloromercurimethyl-4-methyl-1,2-dihydro-benzofuran and 100 cc. of absolute alcohol was placed in a 200 cc. round-bottom flask and refluxed with 1.5 g. of sodium in the form of a 3% amalgam in exactly the same manner as directed for 1-chloromercurimethyl-1,2-dihydro-benzofuran in the preceding paper.² The product was purified by crystallization from ether. The yield was 5.5 g. of pure white crystals, or 35%; m. p., 89.5° .

Analysis. Subs., 0.2174: 15.07 cc. of 0.02618 N AgNO₅. Calc. for $C_{20}H_{22}O_2Hg$: Hg, 40.53. Found: 40.37.

Reaction of 1-Chloromercurimethyl-1,2-dihydro-benzofuran with Methyl Iodide and Acetyl Chloride.—A mixture of 10 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran and 10 g. of methyl iodide in 75 cc. of absolute alcohol was refluxed for 4 hours. As the mixture cooled, 93% of the unchanged chloromercurimethyl compound crystallized.

A mixture of 10 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran and 2.2 g. of redistilled acetyl chloride in chloroform was refluxed. After the solution had cooled, the precipitate that formed was found to consist of 9.6 g. of the unchanged chloromercurimethyl compound.

Reaction of 1-Chloromercurimethyl-1,2-dihydro-benzofuran with Bromine.—A suspension of 10 g. of 1-chloromercurimethyl-1,2-dihydro-benzofuran in 50 cc. of carbon tetrachloride was made, and 4.5 g. of bromine in carbon tetrachloride solution was added slowly at 0° to 5°. The bromine was decolorized immediately, and no evolution of hydro-bromic acid was noted. The mixture was filtered and the precipitate washed with a little carbon tetrachloride and dried. The weight of the precipitate was 7.8 g. corresponding to a 91% yield based on the amount of mixed chloride and bromide of mercury. The carbon tetrachloride solution was evaporated on the water-bath, when there was obtained 5.7 g. or 96% of the calculated amount of light brown, viscous oil, which boiled at 140–143° (20 mm.), showing it to be 1-bromomethyl-1,2-dihydro-benzo uran. 11

When more than 4.5 g. of bromine was added, hydrogen bromide was evolved, and a total of 4 atoms of bromine was absorbed before immediate decolorization ceased, indicating bromination in one position in the ring. No attempt was made to identify the bromination product.

Solution of 1-Chloromercurimethyl-6-carboxy-1,2-dihydro-benzofuran in Sodium Hydroxide.—A suspension of $0.3185\,\mathrm{g}$. of the 6-carboxy compound in 50 cc. of water was titrated with $0.103\,N$ sodium hydroxide solution. For complete solution $15.2\,\mathrm{cc}$. was required. A faint alkaline reaction to litmus resulted. This is almost exactly 2 molecular equivalents of sodium hydroxide. Upon titration of the solution with $0.0952\,N$ hydrochloric acid, no permanent precipitate was observed until $8.2\,\mathrm{cc}$. (8.1 cc. = 1 molecular equivalent) had been added. After a total of $16.5\,\mathrm{cc}$. had been added, precipitation was complete and the solution was filtered. The filtrate contained no mercuric ions.

Methyl Mercuric Hydroxide from Methyl Mercuric Chloride and Sodium Hydroxide.—A solution of 10 g. of methyl mercuric chloride in 75 cc. of warm absolute

¹¹ Adams and Rindfusz, This Journal, 41, 655 (1919).

methyl alcohol was treated with 1.6 g. of sodium hydroxide in 16 cc. of absolute methyl alcohol. An immediate precipitate of sodium chloride was formed. An equal volume of dry ether was added to complete the precipitation of the sodium chloride and the mixture filtered. The precipitate weighed 2.4 g. which is 100% of the calculated amount of sodium chloride. Upon evaporation of the ether and alcohol from the filtrate at room temperature in a vacuum there remained 8.3 g. of grayish-white crystals which melted at 95° after one precipitation from methyl alcohol by means of ether, proving the product obtained to be methylmercuric hydroxide. Dil. hydrochloric acid converted the hydroxide instantaneously into methylmercuric chloride.

4-Allyloxy Methyl Cinnamate: (p)CH₂—CH—CH₂OC₆H₄CH—CHCO₂CH₃.—A mixture of 25.3 g. of the methyl ester of p-cumaric acid, ¹³ 18 g. of allyl bromide, 21 g. of anhydrous potassium carbonate and 30 g. of acetone was refluxed on the steam cone. The completion of the reaction was determined by withdrawing a sample, diluting it with ether, extracting this with dil. sodium hydroxide solution and neutralizing the sodium hydroxide layer with dil. hydrochloric acid. A precipitate indicated the presence of unchanged p-cumaric acid. When the mixture was poured into 400 cc. of cold water the 4-allyloxymethyl cinnamate separated and was recrystallized from 80% alcohol. The yield was 22.5 g. or 73%. The material formed white, glistening plates melting at 65.5°.

Analysis. Subs., 0.3231: 495.8 cc. of CO_2 (25.5°, 725.9 mm.). Calc. for $C_{13}H_{14}O_3$: C, 71.52. Found: 71.83.

3-Allyl-4-hydroxy Methyl Cinnamate: $3-(CH_2-CHCH_2)4-(HO)C_0H_3CH-CHCO_2-CH_3$.—When 8.5 g. of the allyl ether of methyl p-coumarate was heated under a reflux condenser in an oil-bath for 2 hours at 230–245°, rearrangement took place. The ambercolored residue was dissolved in ether, extracted with 10% sodium hydroxide solution and the alkaline solution run into dil. hydrochloric acid at 0° . 3-Allyl-4-hydroxy methyl cinnamate separated as a brown, soft mass which gradually hardened after a few hours' exposure to the air. This substance was not purified further but was used directly in the preparation of the free acid. The yield was 7 g. of crude material.

3-Allyl-4-hydroxycinnamic Acid, 3-(CH₂=CHCH₂)4-(HO)C₆H₃CH=CHCO₂H.—A solution of 4 g. of the crude 3-allyl-4-hydroxy methyl cinnamate in 25 cc. of 10% sodium hydroxide solution was refluxed gently for 4 hours. The mixture was then poured slowly into dil. hydrochloric acid at 0°. The precipitate was filtered, washed with water, dried, dissolved in ether and extracted with 10% sodium bicarbonate solution. The aqueous solution was poured into cold dil. hydrochloric acid solution and the precipitate recrystallized from 80% alcohol. The yield was 2.1 g. of pure white crystals, m. p. 169°, and 0.5 g. of impure crystals, or a total of 63%.

Analysis. Subs., 0.2409: 361.2 cc. of CO_2 (25.5°, 725.9 mm.). Calc. for $C_{12}H_{12}$ - O_3 : C, 70.57. Found: 70.22.

Summary

- 1. The addition of mercuric salts to o-allylphenols has been shown to be a general one. Several substituted o-allylphenols have been treated with mercuric salts with the formation of mercurated-methyl-1,2-dihydro-benzofurans.
- 2. The reactions of these compounds have been extensively studied and compared with the reactions of alkyl mercuric halides and compounds from mercuric salts and olefins.
 - 3. The 1-acetoxy- or 1-halogen-mercurimethyl-1,2-dihydro-benzofurans
 - 12 Sneed and Maynard, This Journal, 44, 2946 (1922).
 - 13 Fischer and Nouri, Ber., 50, 619 (1917).

react with alcoholic or aqueous sodium or potassium bromide or iodide to give the corresponding bromo- or iodomercuri compounds; with alcoholic potassium cyanide and alcoholic potassium thiocyanate, to give the corresponding cyanomercuri or thiocyanatemercuri compounds. In none of these reactions was it possible with excess of reagent to convert the compounds into mercury-bis derivatives.

- 4. The 1-chloromercurimethyl-1,2-dihydro-benzofurans react readily with potassium or sodium hydroxide in alcohol to give the corresponding hydroxymercuri compounds and sodium or potassium chloride. The method is apparently general for alkyl mercuric chlorides since methyl mercuric chloride was converted to methylmercuric hydroxide by a similar procedure. The 1-hydroxymercurimethyl-1,2-dihydro-benzofurans react with acids to form the corresponding salts and, in general, show the typical reactions of any of the known hydroxymercuri compounds.
- 5. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with sodium stannite to give a quantitative yield of the corresponding allylphenol and metallic mercury.
- 6. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with ammonium sulfide, potassium hydrosulfide or hydrogen sulfide in dil. acid solution to give quantitative yields of the corresponding allylphenols and mercuric sulfide.
- 7. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with sodium thiosulfate to give 1-sodiumthiosulfate-mercurimethyl-1,2-dihydro-benzofurans which are unstable compounds decomposing readily into mercuric sulfide and the corresponding allylphenol.
- 8. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans react with sodium amalgam and alcohol to give the corresponding mercuri-bis compounds.
- 9. The 1-halogen-mercurimethyl-1,2-dihydro-benzofurans do not react with methyl iodide or acetyl chloride.

URBANA, ILLINOIS

NEW BOOKS

History of Chemistry. By Francis Venable, LL.D. D. C. Heath and Company, Boston, New York, Chicago, 1922. vii + 168 pp. 19 × 13 cm. Price, \$1.60.

The perusal of this little volume has brought genuine pleasure to the reviewer. The author's profound knowledge of his subject and his long experience as a teacher have enabled him to present the essentials to the earnest student in such a simple and attractive fashion that these essentials will be readily grasped and easily understood.

To teachers, in the exposition of the history of chemistry, this little book will serve as a nucleus about which to develop a more comprehensive course. It is, indeed, a book full of texts, upon any one of which splendid elaborations are readily possible.

The layman also will find in it things he will wish to know regarding the gradual development of the science which, in the process of its upbuilding, has touched him on so many sides.

The first edition of the book appeared in 1894, followed by many more until the present one, which has been entirely re-written and now appears in a new dress, covering the great advances made in the science in the years which have elapsed since it first ventured forth as an American contribution in this interesting field.

EDGAR F. SMITH

Thermodynamics and the Free Energy of Chemical Substances. By Gilbert Newton Lewis, Professor of Chemistry in the University of California, and Merle Randall, Associate Professor of Chemistry in the University of California. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York City; 6 and 8 Bouverie Street, E. C. 4, London; 1923. xxiii + 653 pp. Illustrated. 23.5 × 15 cm. Price \$5.00.

Thermodynamics, as sciences go, is venerable. The patient labor of a multitude of students and the genius of many great minds have given to it a generality, a simplicity, and a refinement of form which constitute beauty. Although austere in aspect by reason of this very perfection, thermodynamics is none the less a handy tool for daily use, a succinct language and an illuminating philosophy of natural science. As the authors of this book say in their dedication, "The fascination of a growing science lies in the work of the pioneers at the very borderland of the unknown, but to reach this frontier one must pass over well travelled roads; of these one of the safest and surest is the broad highway of thermodynamics." Finally, thermodynamics though venerable is still rapidly growing, and its new advances promise an even wider outlook and greater usefulness.

This treatise by Lewis and Randall succeeds to a remarkable degree in presenting, with elegance and yet with freshness, all these aspects of thermodynamics. It is not a textbook in the ordinary sense of the term. As the authors say, "Our book is designed rather as an introduction to research, and as a guide to anyone who wishes to use thermodynamics in productive work." It is divided into three parts, "of which the first treats of the foundations of thermodynamics, the second deals with the special methods of applying the fundamental principles to chemical problems, and the third is devoted to a systematic consideration of the data of thermodynamic chemistry."

The authors use very little mathematics and, besides, give a clear preliminary exposition of this, so that the non-mathematical reader need have no fears. The authors have made such a sane and illuminating statement on this subject that it is worth quoting in full,

This book is the fruition, or culmination of a long series of brilliant researches which Lewis and his students or collaborators have carried out, and which already have been, for the most part, published in This Journal. Naturally, therefore, the authors have drawn largely upon these researches for the illustration and elucidation of their theories. Indeed, we can imagine that Europeans, not appreciating this, may feel that their own achievements have been given too scanty recognition; but this should serve as a useful corrective to many French and German treatises which leave the reader with the impression that the science under discussion is an exclusively Gallic or Teutonic one!

To facilitate mastery of the subject by the isolated and independent student, numerous problems, many of a numerical nature, have been introduced. This is excellent pedagogy. I regret that the authors have not given answers to the numerical problems, for it is my experience that the confidence which a student gains from knowing that he has achieved the correct solution of a problem is of very great value.

"Thermodynamics" is a capital book; clear, vigorous, convincing, and interesting. It is alive throughout with scientific curiosity and enthusiasm. It will broaden the insight and heighten the ardor of its readers. It will be a guide and an inspiration.

ARTHUR B. LAMB

Chemistry. The Science of Matter and its Changes. By HIPPOLYTE GRUENER, Professor of Chemistry, Western Reserve University. Harper and Brothers, New York and London, 1922. 384 pages. Illustrated. 20 × 13 cms. Price \$3.00.

The publishers' notice says that "this volume is one of a new series which will be devoted to scientific subjects of interest to everyone, treated in a clear and readable manner." The author has succeeded in giving a clear and readable general view of the whole scope of chemistry. The last nine chapters in particular, which deal with such subjects as Geo-Chemistry, the Organic Chemical Industries, Sanitary and Agricultural Chemistry, etc., could be read with profit and would be read with interest by any intelligent non-chemist.

It is a tour de force to cover the entire subject of chemistry in a book of this size, and the book suffers, as might be expected, from the omission of important facts and from over-simplification of statement. The discussion of nitrogen fixation is inadequate, the Bucher process is not mentioned, and the diagram which illustrates the Nitrogen Cycle in Nature is not as clear or as complete as others which we have seen. Confronted with the statement (p. 111) that "matter is indestructible, for the atom never changes," one understands the for to mean because and is tempted to object "Nay, that follows not." Moreover, we question the truth of the premise. The statement (p. 309) that the polariscope "is a physical instrument which gives us a glimpse of the internal structure of the molecule" gives an entirely false notion of the uses of the instrument.

The information in the book has not been assembled in a manner to take best advantage of the psychology of the reader. While the first few chapters deal clearly and in a simple and readable fashion with the nature of chemical changes, with the conduct and structure of matter, with oxygen, hydrogen, and water, they deal with them ex cathedra and the reviewer found himself constantly pausing to ask "How do we know this?" "What is the evidence?" And it may fairly be expected that the uninstructed but ready-to-be-interested reader will fail to react cordially to cold information in the absence of the intriguing thinking by which it is deduced. The statement (p. 169) that "antimony is used in alloys to give hardness" and that "its compounds are used to some extent in the match industry and for giving certain qualities to rubber" would be much more interesting, and no more difficult to understand, if the particular alloy were specified and the particular compound for the special purposes. In speaking of platinum, the observation (p. 173) that "many a crucible has been ruined because the operator assumed that platinum was inactive to everything" would have some value if the substances which attack platinum had only been named. One other instance (p. 223): the author speaks of the meaning of the term carbohydrate, carbon and water, and adds that "this composition, however, is only apparent." His failure to mention the sirup and sulfuric acid experiment is another lost opportunity to increase the interest of his account.

The author's effort to treat chemistry in a simple fashion has had the fortunate consequence that the book contains many valuable suggestions for the teacher. His treatment of normal solutions and of the periodic law is excellent. His distinction between aliphatic and aromatic compounds (p. 234) would be of use in the class room—"Paraffin hydrocarbons are little reactive, but the carbon nucleus is rather easily disintegrated. Benzenes are reactive in that they readily form derivatives, but the carbon nucleus is a very stable one, persisting through a great variety of reactions." An ideal is set up by his statement (p. 297) that "it is the work

of physical chemistry to acquire the necessary data by careful measurement, and from them to derive the laws and theories by which we weave the whole together."

The book is well printed. We have found no typographical errors. The full page pictures are well done and generally represent some technical application of the science. The lack of an index will probably be felt by the reader who is not a chemist. The glossary at the end of the volume contains some excellent definitions, all of them in simple language, and could be studied with advantage by teachers of chemistry. The book will be of interest to educated people who are not chemists, and ought to fill a real want with high school students who wish for something to read beyond their textbook.

TENNEY L. DAVIS

Atomic Form with Special Reference to the Configuration of the Carbon Atom. By EDWARD E. PRICE. Longmans, Green and Company, 39 Paternoster Row, London, E. C. 4; 55 Fifth Avenue, New York; Toronto; Bombay, Calcutta and Madras, 1922. xi + 140 pp. 64 figs. 19 × 12 cm. Price \$1.75 net.

This book is a presentation of what the author calls "The Theory of Atomic Form." The assumptions are made at the start (1) that every carbon atom has the shape of a tetrahedron, each face of which is an isosceles triangle whose altitude equals its base, and (2) that two atoms (of carbon or other elements) may be bonded to one another by having a face in common.

A few of the startling conclusions reached by the author, in attempting to make the facts accord with these hypotheses, are the following: that double and triple bonds do not exist; that mellitic acid has the structural formula,

that the "methane carbon" in triphenylmethane is attached to but one of the three phenyl groups; that the accepted explanations of the stereoisomerism of such compounds as the malic and tartaric acids are all wrong; and that cyclohexane is a cyclic compound, but cyclopropane, cyclobutane, cyclopentane, cycloheptane, and cyclo-octane are not. Mention is not made of the fact that the theory would necessitate large numbers of isomers which have not been found (such as two isomers of any compound of the general formula H₂CA₂, and three of H₂CAB), nor of the fact that the structures he assumes for the diamond and for graphite are not in agreement with the results of X-ray analysis. Of the facts "explained" by this theory, the reviewer has been able to find none which are not better and more simply accounted for on the basis of the ordinarily accepted ideas.

A model of the benzene nucleus is proposed in which there are 12 exposed faces, 6 above and 6 below the plane of the "Benzenoid." To account for the fact that hydrogens are attached to only 6 of these faces, the author writes:

"It is assumed that the figures of Carbon and its compounds when in the gaseous state are floating in a medium which supports them in much the same way as water supports any objects floating in it, and that the molecules are subject to the same laws of gravity and mutual attractions as are observable in other and larger objects. If it be allowed that the Hydrogen Atom has the form of a very oblate pyramid, it will follow that nascent Hydrogen will adopt a position in which the base of the pyramid will be above and the apex will occupy the lower position.

"In this position the Hydrogen Atoms will readily combine with the lower surface of the Benzenoid, but it will be practically impossible for them to make stable attachments to the upper surface; to do so it would be necessary for the Hydrogen to make a complete inversion of its position so that the base may be below and the apex above, such a change of position would be unlikely. In this view, it would be the *upper* surface of the Benzenoid which would be free from Hydrogen."

The author makes absolutely no use of any of the developments of the past 25 years in the field of atomic and molecular structures.

The book is written in a clear, readable style, and is well illustrated with many diagrams and photographs.

MAURICE L. HUGGINS

Catalysis in Organic Chemistry. By Paul Sabatier, Dean of the Faculty of Sciences of Toulouse. Translated by E. Emmet Reid, Professor of Organic Chemistry, Johns Hopkins University. D. Van Nostrand Company, 8 Warren Street, New York, 1922. xxiv + 406 pp. 23.5 × 15.5 cm. Price \$5.00 net.

Dr. Reid purported to translate the 1920 edition of Professor Sabatier's book but gave us a volume that has all of the many good points of the original with several invaluable ones added. The chief worth of the second French edition, which is approximately a half larger than the 1913 edition, lies neither in the theoretical treatment nor in the critical judgment of experimental results, but in the assembling of a great many scattered references and observations on the subject of catalysis in organic chemistry by the man who is preëminent in this field. To list the subjects treated in the book would be but to itemize the fundamental reactions of organic chemistry, since almost all are subject to the influence of catalysts. It was to be expected that more space would be devoted to heterogeneous

catalysis and specifically to hydrogenation than to other phases of the subject. One may pick out topics such as the use of copper in the Ullmann reaction which are inadequately treated, but in general the book is well balanced and is a veritable storehouse of facts comparable to Dr. Bancroft's book on Colloids. Dr. Reid has given an excellent translation and has added references to the literature of 1920–22 and many pages of footnotes by himself and others which contain important, interesting, and otherwise unpublished information. These footnotes give a little of that critical examination of the literature which is so greatly needed in the field covered by this book.

The usefulness of the French edition is restricted because it lacks an author or subject index. Dr. Reid at the expense of a great deal of labor has devoted 56 pages to a subject index having some 7000 entries and an author index of 1100 names.

A 2-page sketch of Professor Sabatier's life by the translator and a 12-page article by Dr. Wilder D. Bancroft on "Theories of Contact Catalysis" have been added.

A rapidly widening circle of chemists will find that they owe a great debt of gratitude to Professors Sabatier and Reid for having brought together in a well indexed, convenient, and suggestive form the material contained in this book.

HOMER ADKINS

Organic Chemistry or Chemistry of the Carbon Compounds. By Victor von Richter. Edited by Professor R. Anschütz and Dr. H. Meerwein. Vol. III. Heterocyclic Compounds. Translated from the eleventh German edition, by E. E. Fournier D'Albe, D.Sc. P. Blakiston's Son and Company, 1012 Walnut Street, Philadelphia, 1923. xviii + 326 pp. 22.5 × 15 cm. Price \$6.00 net.

With the publication of Volume III (Heterocyclic Compounds) of Victor von Richter's "Organic Chemistry" the complete translation of the eleventh German edition (published in 1913) of this well-known text and reference book is now available. The English translation has appeared in three volumes whereas the German edition appeared in two volumes, the second covering both carbocyclic and heterocyclic compounds. This book is so well known and has been so useful to organic chemists for general reference that it is hardly necessary to mention that Volume III describes the chief compounds and reactions of all except the rarest classes of heterocyclic compounds.

As mentioned in the review of Volume II of the English translation [This Journal, 44, 2067 (1922)], it is regretable that a book which has required so much time and expense in preparation should be 10 years old in subject matter, at its date of appearance. In spite of this fact, all organic chemists will welcome the completed English edition.

Hexosamines, Their Derivatives, and Mucins and Mucoids. By P. A. Levene, M.D. Monograph No. 18. The Rockefeller Institute for Medical Research, New York, 1922. 104 pp. 25 × 17.5 cm.

The monograph is a review of a narrow field of organo-biological chemistry by one of the world's foremost organic chemists who has devoted his time to the organic chemistry of biological products. The purpose of the author as stated in the preface is not to offer a complete review of all the literature on the subject but to bring together that part of it which has appeared from his laboratory in the course of many years.

Of the two sections of his work, the first is devoted to the 2-amino-hexoses and their derivatives and was undertaken with the object of procuring data for the purpose of identification of these compounds. The question as to the configuration of carbon atom 2 cannot as yet be answered by direct chemical evidence and, therefore, the use of indirect evidence is justified. The indirect evidence from his own and the work of others is presented. The experimental part consists of experiments on the (1) conversion of hexosaminic acids into their epimers, (2) preparation of hexosaminic acid from 1-aminopentosides, (3) synthesis of hexosamines, (4) 2-5-anhydro-pentoxycaproic acids, (5) 2-5-anhydro-tetroxyadipic acids, (6) chitose and epichitose, and (7) 3-aminoheptonic acids.

Part 2 deals with the mucins and mucoids and in particular with available data and experimental work on chondroitin-sulfuric acid and mucoitin-sulfuric acid, together with a discussion of the distribution of acids of various types in organs and tissues.

W. R. BLOOR

Injury, Recovery and Death, in Relation to Conductivity and Permeability. By W. J. V. OSTERHOUT, Professor of Botany at Harvard University. Monographs on Experimental Biology. J. B. Lippincott Company, Philadelphia and London, 1922. 259 pp. 96 fig. 21 × 14 cm. Price \$2.50.

The volume is noteworthy for two things: (a) The quantitative study of rates in the processes occurring in living matter; (b) the development of precision in the definition of such concepts as life, vitality, injury, recovery and death. Due in part to a fortunate choice of experimental material the author has succeeded in studying processes in vita which had formerly been known chiefly in vitro. The discussion of the problems rests on the assumption that the processes which occur in the organism may be represented by a simple catenary system which obeys the laws of chemical dynamics. The data justify the assumption that life processes consist largely of a series of consecutive unimolecular reactions.

Much of the discussion is based upon changes in permeability of the protoplasm to ions. The permeability is computed from the electrical resistance of the tissues, although other means of determining permeability are also used. Permeability is assumed to be dependent upon the amount

of some substance, M, which is formed by the breaking down of a substance, A, and in turn breaks down continually into another substance, B, according to the scheme, $A \longrightarrow M \longrightarrow B$.

The system for marine plants is in equilibrium in sea water; M is renewed as fast as it breaks down. If the velocity of the first reaction be increased, the amount of M will be increased; if the velocity of the second reaction be increased, the amount of M will diminish. When the resistance of the tissue falls to 10% of its original value, death ensues. If tissue be transferred from a toxic solution to sea water before the resistance has fallen too low, recovery occurs, but recovery is incomplete unless the fall of resistance was very slight. The author advances the view that the death process is always occurring, even in an actively growing cell, and produces no untoward effects unless unduly accelerated by an agent which upsets the normal balance and produces such injury that the life process is terminated.

The concepts of all other workers on the nature of cell permeability are regarded as faulty and are discarded. The author assumes that permeability is governed by the amount of a hypothetical combination between various ions and some constituent of the protoplasm. In the case of cells bathed by a solution containing sodium chloride and calcium chloride, the compound is supposed to have the formula, Na₄XCa, in which X represents some constituent of the protoplasm. Further assumptions are made concerning the amounts of Na₄XCa which will be found when cells are immersed in varying proportions of salt and calcium chloride.

Contemporary students of the physico-chemical problems of living matter find no little difficulty in relating Osterhout's assumptions to the principles of physical chemistry on one side, or to biological principles on the other. The discussion is devoted mainly to injury, death and recovery, but is not correlated with the processes upon which the continuance of life depends such as the absorption of water and of solutes from solutions having concentrations comparable to those from which terrestial plants obtain their nutrients. We cannot lightly assume that there is any sharp boundary between these phases of biological dynamics. In view of the relation between the colloidal state and the absorption of water, it would have been advantageous to have had a discussion of their role in determining permeability.

The work constitutes an advance in the analysis of an important problem in biology which workers in that field cannot afford to overlook.

H. S. REED

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[Contribution from the Kent Chemical Laboratory of the University of Chicago¹]

ABSORPTION SPECTRA OF NITROSYLSULFURIC ACID AND OF THE COMPLEX COMPOUNDS OF COPPER SULFATE AND OF FERROUS SULFATE WITH NITRIC OXIDE^{2,3}

By H. I. Schlesinger and Albert Salathe Received September 1, 1922

In the argument with which Raschig supports his theory⁴ of the chamber process for the manufacture of sulfuric acid, his view that nitrosylsulfuric acid is stable only in solutions containing more than 80% of sulfuric acid plays an important role. The evidence for this view lies in the production of the blue substance, considered by him to be nitrosisulfonic acid (H₂S-NO₅), by reduction of nitrosylsulfuric acid with mercury (a reaction that takes place only in solutions containing more than 80% of sulfuric acid) and in the failure to obtain this blue substance by action of sulfur dioxide on nitrosylsulfuric acid in such solutions. The fact that mercury does not produce the blue color in the more dilute solutions is taken as evidence that these solutions contain no nitrosylsulfuric acid; the fact that sulfur dioxide gives rise to the blue color only in the more dilute solutions is believed to demonstrate that sulfur dioxide reacts only with nitrous acid and not with nitrosylsulfuric acid to yield nitrosisulfonic acid, and that in the more dilute solutions all of the nitrosylsulfuric acid has been hydrolyzed to ni-

- ¹ The experimental work for this paper was carried out by Dr. Salathe at the Research Laboratory of the General Electric Company at Schenectady.
- ² The work herein reported constitutes the Dissertation presented to the Graduate School of the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy.
- ² Presented at the Intersectional Meeting of the American Chemical Society, Evanston, Ill., March 11, 1922. *Chem. Bull.*, 9, 89 (1922).
 - ⁴ Raschig, Z. angew. Chem., 18, 1281 (1905); J. Soc. Chem. Ind., 30, 166 (1911).

trous acid. Generally, however, the formation of the blue substance itself is not relied upon because it is too unstable. Addition of copper sulfate (or ferrous sulfate) which intensifies the color reaction is made use of on the assumption that the intense coloration produced under these conditions is due to the formation of a copper (or ferrous) salt of nitrosisulfonic acid. Upon the basis of this evidence Raschig concludes that nitrosylsulfuric acid cannot exist in the presence of sulfuric acid of concentrations such as are found in the lead chambers and that therefore it cannot be an intermediate in the chamber process. After thus ruling out nitrosylsulfuric acid, he develops from other experimental evidence his theory that the formation of the blue "nitrosisulfonic acid" is the important step in the reactions which finally result in the formation of sulfuric acid.

Raschig's views concerning the stability of nitrosylsulfuric acid have already received rather cogent criticism from two sources. Reynolds and Taylor⁵ have shown that by evaporation of solutions of 60-80% sulfuric acid containing nitrites, crystals of nitrosylsulfuric acid can be obtained. They therefore conclude that the latter must be stable in these solutions. While our work has confirmed their conclusions fully, we were of the opinion that their results might have been open to another interpretation and that further confirmation was desirable. In the second place, Manchot⁶ has called attention to the fact that the blue coloration produced when copper sulfate is used in the reactions described above and used by Raschig as a test for the presence of nitrosylsulfuric acid, might readily be due to the formation of the deep violet complex salt of copper sulfate and nitric oxide, a salt analogous to the similar well-known complex salt of ferrous sulfate and nitric oxide. If Manchot's contention is correct, Raschig's color reaction has no necessary bearing on the question of the presence or formation of nitrosylsulfuric acid. This phase of the problem will receive further consideration later.

In the first part of this paper we are reporting the results of an investigation of the absorption spectra of nitrosylsulfuric acid dissolved in sulfuric acid of various concentrations. From the data obtained it is possible to conclude definitely that the nitrosylsulfuric acid is not completely hydrolyzed until the concentration of the sulfuric acid, used as solvent, has been lowered to 40% by addition of water. It therefore follows that Raschig's criticism of the older theory of the chamber process on the ground of instability of nitrosylsulfuric acid is unjustified. With his other arguments this paper does not deal, except that in the second part some preliminary data bearing on the nature of "nitrosisulfonic acid" are presented.

The absorption spectra of the solutions were examined with a quartz spectrograph of high accuracy. A spark discharge between carbon electrodes impregnated with oxides

Reynolds and Taylor, J. Soc. Chem. Ind., 31, 367 (1912).

⁸ Manchot, Z. angew. Chem., 24, 13 (1911).

of molybdenum and uranium served as the source of light. Time of exposure varied for different types of solution from 30 to 45 seconds except for some of the most opaque solutions for which 90 seconds or more were required.

The solutions were contained in cells such as described by Baly. The windows were of quartz. The bulb was placed as near the end of the outer tube as possible to allow entrance of an inlet tube carrying nitric oxide for the experiments to be described in Part II. In the experiments with nitric oxide, the neck of the bulb was fitted with a 2-holed stopper in order to make it possible to keep the solution continuously saturated with the gas. Rubber tubing, 37 mm. in diameter, such as is used with Gooch crucibles, was employed to join the inner and outer tubes in the usual way. This tubing was found to lose its elasticity on subjection to the action of acid mixtures containing 75% of sulfuric acid and upwards, but to be singularly live after having been subjected to the action of weaker acids for considerable periods of time. The quartz windows were joined to the glass by means of water glass. This, if properly applied, will hold against concd. and dil. sulfuric and nitric acids for hours. After each experiment, the cells were immersed in lukewarm water, and in about half an hour the cement had dissolved and both quartz and glass were then thoroughly cleaned and made transparent by immersion in very dilute hydrofluoric acid.

The curves for the spectra are plotted in the usual way, with oscillation frequencies⁸ as abscissas and logarithms of thickness in millimeters as ordinates. In many cases, however, no reference concentration is given because the concentration of the absorbing substance is not known. The usual method of procedure was followed in making the photographs: first a photograph of the scale was taken, then a photograph of the whole spectrum through the empty Baly tube, then photographs of the absorption spectra of the solution and, finally, another photograph of the thinner layers of the solution. In this way the possibility of contamination of the solutions by the cement or the rubber was tested and excluded. Blank tests with sulfuric acid alone confirmed this observation.

I. Absorption Spectra of Solutions of Nitrosylsulfuric Acid in Sulfuric Acid of Various Strengths

The nitrosylsulfuric acid was prepared by the method of Weber.⁹ Further details of the method of preparation will be found below in connection with a discussion of the effect of impurities on the spectra. A series of $0.1\,N$ solutions was prepared by dissolving the solid nitrosylsulfuric acid in 95.6%, 88.1%, 80%, 70%, 60%, 50% and 39.6% sulfuric acid. Two solutions, one in 93.1% and the other in 74.3% sulfuric acid, which were $0.025\,N$ with respect to nitrosylsulfuric acid were examined and are included in the figure with the $0.1\,N$ solutions. Fig. 1 represents the spectra of all of these solutions, plotted in the usual way and referred to $0.1\,N$ solutions as standard.

There are two striking phenomena exhibited in Fig. 1. In the first place there is the increased ultraviolet absorption, or shift of end absorption toward the visible, with decrease in concentration of sulfuric acid used as solvent. In the second place there is the appearance of an absorption band in the ultraviolet as the concentration of the sulfuric acid approaches

⁷ Uhler and Wood, Carnegie Inst. Pub., 1907, 69.

⁸ Wave number per mm.

⁹ Weber, J. prakt. Chem., [1] 97, 489 (1866).

40%. The incipiency of the band is noticeable at 50%, while at 39.6% acid the band is well defined. The interpretation of these phenomena is that the end absorption is due to nitrosylsulfuric acid and that the spectrum with the absorption band is due to nitrous acid.

This interpretation is based on the following evidence. The spectrum of nitrites is known. 10 Spectra of potassium nitrite in 39.6% sulfuric acid,

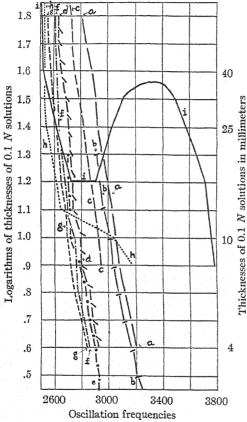


Fig. 1,—Absorption spectra of nitrosylsulfuric acid in sulfuric acid of various concentrations

c = 88.1% f = 70.0% i = 39.6%

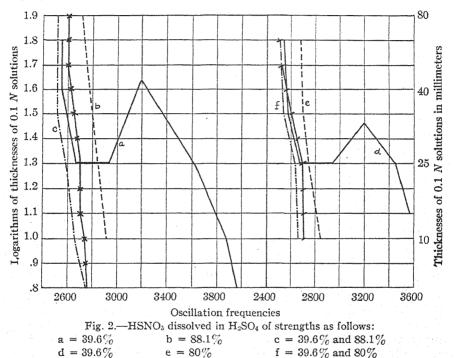
photographed by us, checked with those of aqueous solutions of alkali metal nitrites within the limits of experimental error and are identical with the spectrum of nitrosylsulfuric acid in 39.6% sulfuric acid. It follows, therefore, that in sulfuric acid of this concentration, nitrosylsulfuric acid is completely hydrolyzed to nitrous acid.

Inasmuch as the chemical evidence (slight bubbling and momentary appearance of blue color) showed that this hydrolysis occurs when the sulfuric acid is diluted to 60% while the spectra gave no evidence of nitrous acid at this concentration, it seems probable that the nitrosylsulfuric acid, still undecomposed, blots out the spectrum of the nitrous acid. greater opacity of the former makes this suggestion a very reasonable one, but it was thought best, nevertheless, to prove its correctness experimentally. For this pur-

pose one Baly tube was filled with a solution of 0.1~N nitrosylsulfuric acid in 39.6% sulfuric acid. This solution gives the spectrum of nitrous

¹⁰ Baly and Desch, *J. Chem. Soc.*, **93**, 1755 (1908). In this article the absorption spectrum of nitrosylsulfuric acid will also be found but for only one concentration of sulfuric acid. Our data on nitrites are not reproduced in order to save space.

acid as was made clear above. This tube was preceded by another which contained, in one experiment, $0.1\ N$ nitrosylsulfuric acid in 88.1% sulfuric acid and, in the second experiment, the same concentration of the solute in 80% sulfuric acid. Both of the solutions in the more concentrated acids exhibit the spectrum of the nitrosylsulfuric acid. In order to accommodate the two Baly tubes the source of light was placed $89\ cm$. from the slit and, to allow for the longer distances through which the light had to traverse the solutions, longer exposures were employed. In making the photographs, the length of the column of the solutions in the concentrated acids



was kept constant and the length of the solutions in the dilute acid was varied. If the assumption that the spectrum of the nitrosylsulfuric acid "blots" out that of the nitrous acid is correct, the resulting curves should be like those for a solution of nitrosylsulfuric acid in a concentration of sulfuric acid between 39.6% and that of the stronger acid used. If the decomposition of the nitrosylsulfuric acid is proportional to the decrease in concentration of the sulfuric acid this intermediate concentration of the latter should be the average of the strengths of the weaker and the stronger acids used in the experiment. While there is no reason to believe that this is necessarily the case, the curve for this average concentration is given in crossed lines with the curves for each of the solutions used and with

the curve of the superimposed spectra in Fig. 2. It is seen that while the spectrum of the acid of the average concentration is slightly different from that of the superimposed solutions, the similarity of the two is so great that there can be no doubt of the correctness of the assumption that the spectrum of nitrosylsulfuric acid masks that of nitrous acid. It follows from this that in solutions of sulfuric acid as dilute as 50% there is left undecomposed an appreciable quantity of nitrosylsulfuric acid. In so far as Raschig's criticism of the older theory of the chamber process is based upon his statement that nitrosylsulfuric acid cannot exist in the lead chambers, that criticism is unjustified.¹¹

The data presented in Fig. 2 also aid in interpreting the shifting end absorption observed as the sulfuric acid is diluted from 96 to 60%. The most concentrated solution undoubtedly represents one in which little, if any, of the solute, nitrosylsulfuric acid, is decomposed. But, as the solution becomes more dilute (with respect to the concentration of the sulfuric acid used as solvent), more and more nitrous acid is formed and the absorption due to this substance is added to that due to the nitrosylsulfuric acid left in solution.¹² Since the extent of the decomposition is not known, the curves for the spectra of solutions in sulfuric acid lying between 96 and 39.6% cannot be calculated. It is not likely, however, that the explanation given for the shift in the end absorption can completely account for the phenomenon, because the concentration of the nitrosylsulfuric acid decreases as that of the nitrous acid increases. The phenomenon may in part also be due to the influence exerted by the change in the character of the solvent. Similar shifts have been observed in other solutions, notably by Schaefer in the case of nitric acid dissolved in sulfuric acid. 13 The similarity in the absorption spectra of nitrosylsulfuric acid, just described, and those of nitric acid in varying concentrations of sulfuric acid, described by Schaefer, is too striking to be passed by without comment. In both cases dilution of the sulfuric acid with water causes first a shift in the end absorption toward the visible, and then the gradual appearance of an absorption band. In both cases the band appears at approximately the same concentration.

It was at first thought that this striking similarity might be due to the presence of nitric acid in our nitrosylsulfuric acid. This was suspected al-

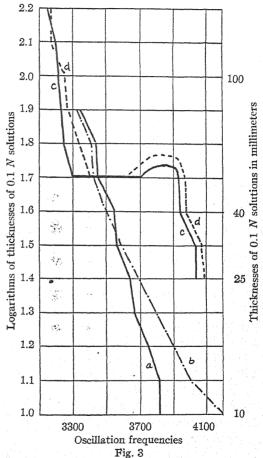
¹¹ While qualitative spectroscopic evidence cannot lead to definite conclusions concerning the relative amounts of nitrosylsulfuric acid and of nitrous acid in these solutions, the fact that the shift in the end absorption is greater when the concentration of sulfuric acid is varied from 100 to 80% than when varied from 80 to 60% suggests that much of the decomposition of the nitrosylsulfuric acid occurs before the concentration of sulfuric acid has been lowered to 80%.

¹² For the theory concerning the effect of two substances on the absorption spectrum of the resulting solution see, for example, Kayser, "Handbuch der Spektroskopie," S. Hirzel, Leipzig, 1905, vol. 3, p. 92.

¹³ Schaefer, Z. anorg. Chem., 97, 285; 98, 77 (1916).

though the end absorption in the nitric acid and the band which develops as the water is added are both found much farther in the ultraviolet region than is the case with nitrosylsulfuric acid. To make sure that this difference in the region of absorption was not due to an error in the scale of wave lengths, either in Schaefer's work or in ours, we made a plate of nitric acid in 39.6% sulfuric acid. Our curve and Schaefer's agree well (See Fig. 3).

Error in scale is, therefore, excluded. In order to make sure that impurities played no role in our spectra of nitrosylsulfuric acid the following solutions were examined. In preparing the substance, the crystals were washed with glacial acetic acid and with carbon tetrachloride in order to dry them rapidly and free them from nitric acid. Examination of solutions of sulfuric acid to which a little carbon tetrachloride and glacial acetic acid had been added, showed that these impurities left the sulfuric acid transparent and that they could not have been responsible for the spectra. The fact that nitric acid is far more transparent than our solutions excludes it as the absorber. Finally, the fact that only nitrosylsulfuric acid could have been responsible for the absorption was demonstrated by photographing spectra of solutions prepared by (a) using the crystals purified



a and b = HNO₃ in 88.1% H₅SO₄; a before, b after gently boiling for $^{1}/_{2}$ hour. c = KNO₃ in 39.6% H₂SO₄, d = KNO₃ in 40% H₂SO₄, after Schaefer

as described above, (b) dissolving pure sodium nitrite in concd. sulfuric acid, (c) dissolving, in sulfuric acid, nitrogen tetroxide prepared in one case by heating lead nitrate and in another by heating copper nitrate. All of these solutions gave absorption spectra which, except for unavoidable

differences in concentration, were identical. The curves are not reproduced in order to save space.

It has thus been shown that the great similarity between the absorption spectra of nitric and of nitrosylsulfuric acids in sulfuric acid of various strengths is not due to any common impurity. It is, therefore, probably due to a common cause, most probably the dehydrating action of sulfuric acid. In the case of the nitrous acid this action results in the formation of the mixed anhydride, nitrosylsulfuric acid. It is possible that with nitric acid a similar anhydride may be obtained or dehydration may proceed as far as nitrogen pentoxide. 14 The latter possibility suggests that a solution of nitric acid in concd. sulfuric acid might readily lose oxygen on account of the great instability of nitrogen pentoxide. If this occurs, nitrosylsulfuric acid must result. Lunge15 states that this is the case and says further "this transformation takes place almost completely after brief boiling" for concentrations of acid of d. 1.71 (78.04%) and upwards. In the spectroscopic method we have a much more accurate means of testing the correctness of Lunge's statement than any means he used. A 0.1 N solution of nitric acid in 88.1% sulfuric acid was prepared and photographed. was then gently boiled during half an hour open to the air and again photographed. Reference to Fig. 3 shows that very little if any nitrosylsulfuric acid was formed, for if it had been formed in even small amount absorption should have been greatly increased; as a matter of fact, the curves show slightly less absorption after boiling the acid, due, no doubt, to a small loss of nitric acid by evaporation. These findings were confirmed by chemical tests which, however, are not as sensitive as the spectra. While this result thus differs from the findings of Lunge, it is possible that the difference may be due to difference in concentration of the nitric acid.

One further suggestion in connection with our curves for nitrosylsulfuric acid is of interest. Since sulfuric acid is transparent in the range of frequencies examined, one might expect its mixed anhydride with nitrous acid to exhibit a spectrum similar to that of the latter. This is not the case; nitrous acid has an absorption band, nitrosylsulfuric acid only end absorption. This may indicate that in the latter there is an NO₂ group, since the evidence is fairly good that in nitrous acid the absorption spectrum is due to the ONO group. This point is not considered definitely proved; too little work on that type of isomerism in inorganic compounds, particularly with reference to absorption spectra, has as yet been done to warrant drawing definite conclusions. Further work along these lines is in progress.

¹⁴ It is also possible that in the solutions in concd. acid a nitrate of sulfuric acid may exist. See Stieglitz, This Journal, 44, 1293 (1922).

¹⁵ Lunge, "Sulfuric Acid and Alkali," D. Van Nostrand Co., 1913, vol. I, part I, p. 343.

¹⁶ Simple anhydride formation usually does not greatly modify the absorption spectrum. See Hantzsch and Scharf, *Ber.*, **46**, 3570 (1913).

It may be added that the nitrosulfonic acid structure for nitrosylsulfuric acid has already received considerable attention.¹⁷

II. Absorption Spectra of the Complex Compounds of Ferrous and of Cupric Sulfate with Nitric Oxide. Comparison of these Spectra with that of Nitrosisulfonic Acid

As has already been mentioned, Manchot⁶ has pointed out that the intensely colored compounds produced by reduction of nitrosylsulfuric acid by mercury in the presence of ferrous or cupric sulfate might be complex salts of the type FeSO₄.NO instead of being nitrosisulfonates as supposed by Raschig. A comparison of the spectra of solutions of the colored compounds prepared by reduction of nitrosylsulfuric acid with those of solutions prepared by passing nitric oxide into the sulfate solutions should afford a means of deciding this question and the necessary observations have. therefore, been made by us. The complex salts of nitric oxide have been studied in detail by Kohlschütter¹⁸ and by Manchot¹⁹ and their work, has shown that there are two classes of compounds of the same composition. In the case of ferrous sulfate, for example, a brown compound is formed when nitric oxide is passed into an aqueous solution of the salt while a deep red compound results from the action of nitric oxide on ferrous sulfate dissolved in concentrated solutions of sulfuric acid. For this reason it seemed necessary to study the absorption spectra of the ferrous sulfate-nitric oxide complexes in sulfuric acid of various strengths. It should be mentioned that Kohlschütter has already reported visual observations of these spectra, but these observations are not sufficiently precise to serve our purpose.20

The apparatus used in this part of our work was the same as that described in the first part of the paper. The nitric oxide was generated from copper pellets and nitric acid, diluted 1:1 with water. The gas was purified by passing it over soda lime, through concd. sodium hydroxide solution and then through concd. sulfuric acid. It is essential that the solutions in which the nitric oxide is absorbed be thoroughly freed from traces of oxygen, since the presence of the latter would give rise to the formation of either nitrosylsulfuric acid or of nitrous acid in the solutions. Each of these

¹⁷ See for example: Raschig, *Z. angew. Chem.*, **18**, 1281 (1905). Lunge, *ibid.*, **19**, 807, 857, 881 (1906). Gerard and Pabst, *Bull. soc. chim.*, [2] **30**, 531 (1878). Riehringers, "Chem. Techn. Unters.," **1917**, p. 25.

¹⁸ Kohlschütter, Ber., (a) **37**, 3044 (1904); (b) **40**, 873 (1907); (c) **44**, 1423 (1911).

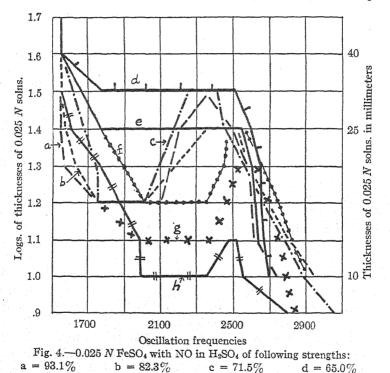
¹⁹ Manchot, Ann., (a) 350, 368 (1906); (b) 375, 308 (1910); (c) Ber., 47, 1601 (1914).
In the last named article a complete list of references to Manchot's work is given.

²⁰ Before publication of this paper, we communicated with Professor Kohlschütter in order to make certain that he would not consider our work an infringement of his field. He not only assured us that this would not be the case but also most courteously put at our disposal some unpublished notes. We take great pleasure in acknowledging his kindness in this matter.

e = 59.4%

substances has an absorption spectrum that would interfere with the absorption spectra to be studied. To exclude oxygen, oxygen-free hydrogen was passed through the solutions until air had been completely removed and the solutions thereafter were not allowed to come into contact with any gas except hydrogen or nitric oxide.

Fig. 4 contains the curves for the compounds of ferrous sulfate and nitric oxide. The solutions were prepared by dissolving the salt in a little water and then adding enough diluted sulfuric acid to the mixture to produce the desired concentration of salt and of acid. After the air had been displaced



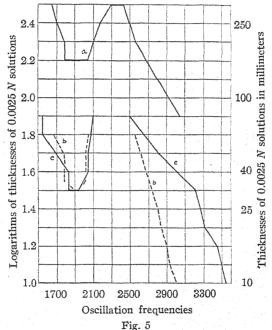
from the solution by hydrogen, the solution was saturated with nitric oxide. The solutions represented by the curves of Fig. 4 were $0.025\,N$ with respect to the iron salt; the strength of the acid was varied from 93.1% to 0%. The absorption spectra of the compound of nitric oxide with ferrous sulfate in 93.1, 82.3 and 71.5% sulfuric acid, respectively, all show an absorption band with head in the frequency interval from about 1750 to 2100; maximum transmission is approximately at 2300. These three curves, in other words, are very similar indicating that in this range of concentration of the sulfuric acid no change has occurred in the nature of the complex salt.

g = 15%

h = 0%

f = 45.0%

The curves for 65.0% and for 59.4% acid are quite different in character. The absorption band is no longer well defined and the region of absorption is much shallower. Further dilution produces still further change. With 45.0% acid there is again an absorption band, similar to the one just described, but its head is now in the frequency interval 2000 to 2400 and maximum transmission has been displaced to 2500. From this concentration of acid to solutions in water, the new absorption band remains unchanged except that it becomes deeper, that is, the solution becomes more opaque in the region of absorption. While the difference exhibited by these various curves is not very great, it is sufficiently definite and occurs at so definite a range of concentrations that it fully warrants the conclusion that there are two compounds, one existing in concd. sulfuric acid and the

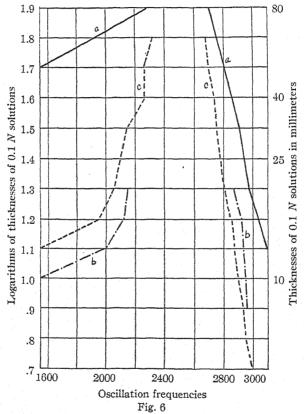


a=0.025~N FeSO4 with NO in 93.1% H_2SO_4 . b= ferrous nitrosisulfonate in 93.1% H_2SO_4 ; Fe = 0.0025 N. c=0.0025~N FeSO4 with NO in 93.1% H_2SO_4

other in dilute acid or in water. As the concentration of the acid is changed from about 65% to about 50%, the one compound is transformed into the other. In the interval between these extremes, both compounds are apparently present and this fact causes the indefiniteness of the character of the curves for 65% and for 59.4% acid. These results corroborate the visual observations of Kohlschütter¹⁸ and the conclusions of Manchot¹⁹ based on chemical evidence but make much more precise the location of the

two bands and show, for the first time, the existence of the definite range of transition.²¹

Fig. 5 was made in order to show the identity of the compound of ferrous sulfate with nitric oxide, formed in concd. sulfuric acid, with Raschig's ferrous nitrosisulfonate. The latter was prepared as follows. Ferrous sulfate was dissolved in water, sulfuric acid was added in sufficient amount to give a strength of 93.1%, and the mixture cooled. Sodium nitrite, finely



a = 0.1 N CuSO₄ with NO in 82.3% H₂SO₄. b = 0.1 N CuSO₄ with NO in 93.1% H₂SO₄. c = Cu nitrosisulfonate in 93.1% H₂SO₄; Cu = 0.1 N

ground and carefully dried, was then added slowly. The mixture was rotated until all of the particles of sodium nitrite had passed into solution. A few drops of mercury were added to this solution and the mixture was violently shaken for about 15 minutes. The characteristic red color developed and deepened during this interval. The concentration of the iron salt in this experiment was $0.0025\ N$ and to make the comparison satisfac-

²¹ Kohlschütter (see Ref. 18 particularly 18c), gives a very well founded theory to account for the existence of these isomers. See also Manchot, Ref. 19c.

tory we prepared the iron compound, described in the preceding paragraph of this concentration also and photographed its spectrum. Curves b and c of Fig. 6 reproduce the experimental results. It is quite clear that Raschig's nitrosisulfonate of ferrous iron and the complex compound of ferrous sulfate and nitric oxide formed in concd. sulfuric acid are identical.²²

Fig. 6 shows that the compound obtained when nitric oxide is passed into copper sulfate dissolved in concd. sulfuric acid is identical with Raschig's nitrosisulfonate of copper. The two compounds were prepared in quite analogous fashion as described for the respective iron salts. Both in the photographs of iron and of copper "nitrosisulfonates," ultraviolet end absorption is superimposed on the spectra of the salts themselves. This is due to the fact that the method of preparation makes the exclusion of nitrogen tetroxide impossible. Furthermore, probably not all of the nitrosylsulfuric acid is reduced. This last fact also makes somewhat uncertain the concentration of the compound; all that can be given with accuracy is the concentration of the original metal salt.

The identity of the nitric oxide complexes with the supposed nitrosisulfonates makes a study of the absorption spectrum of the latter of great interest. Balv and Desch¹⁰ report an observation on copper nitrosisulfonate which agrees well with our data. Kohlschütter and Sazanoff²³ report a visual observation of the free acid which they find to have a spectrum quite different from that of the complex salts. Our investigation by the more exact photographic procedure led to the opposite result as is shown in Fig. 7. Curve a, represents the spectrum of nitrosisulfonic acid prepared as described for its ferrous salt, except that no ferrous sulfate was added. The solution is very unstable and photography difficult.²⁴ Owing to the impossibility of determining whether the reaction of the nitrite with mercury is complete or how much nitrosisulfonic acid has decomposed, it is impossible to say what the concentration of the solution is. The nitrite was used in such concentration as to give a $0.5\ N$ solution. Curve b represents another photograph of the spectrum of the copper salt. The concentration of the reagents here was only 0.1 N because of the greater opacity of the solution. Nevertheless, the actual data are recorded for both curves, since any attempt to recalculate them to a common basis of reference would have been quite arbitrary in view of the uncertainty concerning the concentrations.²⁵ The two curves are seen to be closely similar.

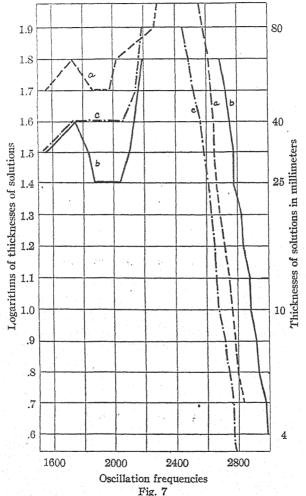
 $^{^{22}}$ Fig. 5 contains also the curve for FeSO₄NO in concd. sulfuric acid, but with an iron concentration 0.025 N. Both curves are referred to the concentration 0.0025 N. It is seen that Beer's law does not hold. This phenomenon will be further investigated.

²³ Ref. 18c. More details are given in the dissertation by Sazanoff (Berne).

²⁴ Exposures of 15 seconds were employed.

 $^{^{25}}$ A second curve for "nitrosisulfonic acid" is shown in "c" of Fig. 7. This solution was prepared by action of sodium sulfite on $0.5\ N$ sodium nitrite dissolved in sulfuric acid in order to avoid the presence of mercury. Curves a and c agree well except for differences due to unavoidable differences of concentration.

Both show an absorption band with head about at 1900 and additional absorption (possibly a second incipient band) in the far red. Another striking point about these curves is that the absorption band is found in the same range of frequencies as is the absorption band for the compound which



a = nitrosisulfonic acid from 0.5 N NaNO₂, H_2SO_4 and Hg. b = the Cu salt of a. c=nitrosisulfonic acid from 0.5 N NaNO₂, H_2SO_4 and Na_2SO_3

ferrous sulfate and nitric oxide form when mixed in the presence of concd. sulfuric acid.

This striking similarity suggests that "nitrosisulfonic acid" is really a complex compound of sulfuric acid and nitric oxide whose formula might be written H₂SO₄.NO. According to this point of view, the supposed com-

plex has a very high dissociation pressure and can be formed only when nitric oxide is generated in contact with sulfuric acid so that there would be a high degree of supersaturation of the former. While Raschig has brought forward a number of experimental facts that tend to prove the correctness of his formulation for "nitrosisulfonic acid," practically all of them accord as well with the view here presented as with Raschig's. The fact that Manchot 19 has been able to prepare a complex compound 26 of hydrogen chloride and nitric oxide, stable only at very low temperatures, favors the point of view here presented.²⁷ The spectroscopic evidence thus far available is not adequate, however, to decide this question definitely and more detailed discussion is, therefore, out of place. Work has already been begun on the study of non-aqueous solutions of the complex compound of ferrous chloride and nitric oxide, on aqueous solutions of nitroso ferrous phosphate containing varying amounts of phosphoric acid and on other nitroso metallic salts by the spectroscopic method in order to obtain further data bearing on this question.28

In conclusion it gives us great pleasure to acknowledge to the Director of the Research Laboratory of the General Electric Company at Schenectady our sincere appreciation of his courtesy in granting to us the use of a room and of the facilities of the Laboratory for carrying out this research. We wish to include in this expression of appreciation all others of the staff of the Laboratory who most kindly aided us in securing apparatus and materials and in many other ways.

Summary

- 1. The absorption spectra of nitrosylsulfuric acid dissolved in sulfuric acid of various concentrations have been obtained. The spectra show that appreciable quantities of the former remain undecomposed when the sulfuric acid is diluted with water to 50% and that, at higher concentrations of the latter acid, relatively large amounts of nitrosylsulfuric acid are present. This finding disproves one of the fundamental assumptions made by Raschig in developing his theory of the chamber process.
- 2. Absorption spectra of the complexes formed by ferrous sulfate with nitric oxide in solutions of sulfuric acid of various strengths have been photographed. The spectroscopic data confirm the view that there are two such complexes, both of the composition FeSO₄.NO, and show that one of them is stable when the sulfuric acid has a concentration above 65% and
- ²⁶ Further information concerning this compound is found in the paper by Rodebusch and Yntema, This Journal, 45, 332 (1923).
 - ²⁷ For a similar view, see Wentzki, Z. angew. Chem., 24, 392 (1911).
- ²⁸ Since the above was written, preliminary experiments have shown that the compound FePO₄.NO is brown in aqueous solution, and red in the presence of concd. phosphoric acid. This is quite definite evidence that the change in spectrum described above in the case of FeSO₄.NO is not related to any special property of the sulfate ion.

the other when the concentration of the acid is below 50%. Spectra of the complex, CuSO₄.NO, have also been obtained and the spectra of these complex salts have been compared with those of the so-called ferrous and cupric nitrosisulfonates and have been found to be identical.

- 3. A preliminary study of the absorption spectrum of "nitrosisulfonic acid" has shown it to be very similar to that of the ferrous sulfate-nitric oxide complex existing in concd. sulfuric acid solution. This finding supports the view that possibly nitrosisulfonic acid should be looked upon as an unstable solution of a complex compound of sulfuric acid and nitric oxide.
- 4. Examination of the spectra of solutions of nitric acid in coned. sulfuric acid, before and after heating the solutions, has shown that nitric acid is not readily decomposed in such solutions into nitrosylsulfuric acid, at least if the solution is not very concentrated with respect to nitric acid.
- 5. The character of the absorption spectrum of nitrosylsulfuric acid favors the view that this substance is present in solution largely as nitrosulfonic acid.

Further work along these lines is in progress. In addition, the investigation is being extended to other acids of sulfur, particularly the polythionates, polysulfides and to acids of sulfur and nitrogen.

CHICAGO, ILLINOIS

[Contribution from the Chemical Laboratory of George Washington University Medical School]

THE ESTIMATION OF SIMPLE, SOLUBLE CYANOGEN COMPOUNDS, MAKING USE OF THE PRINCIPLE OF AERATION

By Joseph H. Roe Received March 21, 1923

The older methods for the estimation of cyanides have their limitations in the presence of interfering substances. When impurities are encountered the usual procedure has been to dissolve the sample, acidify with a mineral acid, distil, and determine the hydrogen cyanide in the distillate. Distillation of hydrocyanic acid from an acidified cyanide solution is objectionable as a quantitative procedure because (1) it involves some loss, because of hydrolysis according to the reaction HCN + $2H_2O \longrightarrow HCOONH_4$; (2) great care must be exerted to prevent escape of hydrogen cyanide during the boiling, as this substance is highly toxic, making distillation undesirable from the point of view of safety to the operator; (3) a cyanide cannot be separated from complex cyanogen compounds such as ferrocyanides by distillation since boiling with an acid decomposes the latter, giving a false yield of hydrogen cyanide: $2K_4Fe(CN)_6 + 3H_2SO_4 \longrightarrow 6HCN + 3K_2SO_4 + K_2Fe_2(CN)_6$. Furthermore, distillation methods are not successful if it is desirable to determine slightly.

dissociable mercuric cyanide in the presence of interfering substance. Because of these limitations, a new method, making use of the principle of aeration, was developed.

Principle.—Hydrocyanic acid can be removed quantitatively from a solution at ordinary temperatures by passing a current of air through the solution for an appropriate time. If free hydrogen cyanide is present, it is thus aerated by means of an ordinary suction pump from one flask into another flask containing a solution of sodium or potassium hydroxide of correct concentration. The sodium or potassium cyanide solution thus obtained in the second flask is then titrated with standard silver nitrate solution using potassium iodide as an indicator (the Denigès modification of Liebig's method). When a cyanide is to be determined, it is dissolved in water, the solution is acidified properly and then aeration into a second flask is carried out, and the cyanide solution finally titrated as described above. This procedure overcomes all the objections to separation of a cyanide from impurities by distillation as pointed out above. The method thus possesses the advantages of being an easy procedure, yielding highly accurate results, and affording entire safety to the operator.

The titration is based upon the principle that when silver nitrate is added to an alkaline cyanide solution, a soluble double salt is formed. AgNO₃ + 2KCN \longrightarrow KAg(CN)₂ + KNO₃. After a few drops of a solution of potassium iodide have been added to the mixture, grayish-white insoluble silver iodide separates when all the cyanide has been converted into the double salt of silver. Potassium iodide thus produces a very sensitive end-reaction, since silver iodide is the most insoluble of all the silver salts. In this process, $1 \text{AgNO}_3 = 2 \text{KCN}$, and 1 cc. of a 0.1 N standard solution of silver nitrate would have the following values: $0.005404 \, \text{g}$. of hydrogen cyanide; $0.013022 \, \text{g}$. of potassium cyanide; $0.009822 \, \text{g}$. of sodium cyanide.

Procedure: For simple, soluble, dissociable cyanides, such as potassium cyanide.—Dissolve a convenient sample, such as 0.050 g. of potassium cyanide, in 100 cc. of water. Prepare apparatus suitable for aeration, as shown in Fig. 1. The double bubble breaker apparatus developed by Folin for determinations of ammonia has been found very serviceable for this work. In Cylinder A place the dissolved cyanide solution with a few added drops of amyl or caprylic alcohol to prevent foaming, and in Cylinder B 100-150 cc. of 5% sodium hydroxide solution. Close the apparatus and start the pump to produce a slow bubbling of air through the flasks. By means of a pipet, introduce into the apparatus at opening of tube marked "E" 25 cc. of saturated (1 g. per cc.) solution of tartaric acid. Adjust the pump until about 3 liters of air per minute passes through the apparatus. This speed is approximated when the films produced by the air bubbles leaving the surface of the fluid in the taller cylinder rise

about 25 mm. above the surface of the liquid. Continue the aeration for 2 to 3 hours. Stop the pump, disconnect the flasks, add 10 drops of 10% potassium iodide solution to flask B and titrate with $0.01\,N$ silver nitrate solution until a faint turbidity appears (as viewed against a dark background). As 1 cc. of $0.01\,N$ silver nitrate solution equals 0.0013 g. of potassium cyanide, the reading of the buret is about 38 cc. and the calculation then is 38×0.0013 or 0.0494 g. of potassium cyanide.

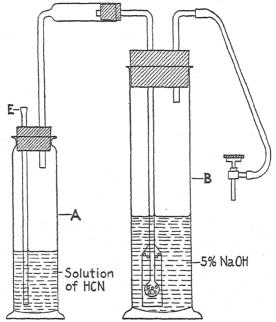


Fig. 1.—Aeration apparatus for determination of hydrogen cyanide

Description and Discussion of the Method

The following factors are of importance.

- 1. Time of Aeration.—Quantitative recoveries were obtained from 2 hours' aeration with a Folin Ammonia Apparatus and a water vacuum pump adjusted to pass about 3 liters of air per minute through the apparatus. It is, therefore, essential to pass 360 to 500 liters of air through the apparatus when analyzing 50mg. samples of cyanide.
- 2. Concentration of the Acid Added.—This must be in excess of the amount necessary to convert all the cyanide present into hydrogen cyanide. Thus in the reaction, $2KCN + H_2SO_4 \longrightarrow 2HCN + K_2SO_4$, it will be seen that very little more than the theoretical amount required for a complete double decomposition is necessary, since hydrogen cyanide is such a weak acid and is constantly being removed from the field, thereby shifting

the equilibrium constant for the reverse reaction towards zero. However, it was found practical to have considerable acid present, since this reduces the time required for aeration; enough acid should be added to make the acid concentration of the solution about 20%; concentrations above this did not interfere with but did not facilitate the process.

- 3. Kind of Acid.—Probably any fairly strong acid could be used. Sulfuric, hydrochloric, and tartaric have been employed interchangeably, and accurate results secured. In practice, tartaric acid was used since it can be added in a highly concentrated form without the production of heat such as occurs when coned. sulfuric or hydrochloric acid is added to the water solution. However, it was found that the heat resulting from the addition of coned. sulfuric acid did not vitiate results, although it caused spattering and vaporization of the liquid not desirable from a mechanical point of view.
- 4. The Concentration of the Alkali.—The concentration of the alkali in the flask into which the hydrogen cyanide is passed is important. If aeration is carried on very slowly but little more than the calculated amount necessary for the neutralization will suffice, but for rapid aeration the solution should contain 100 times the calculated amount. So high a concentration is necessary to prevent the escape of some free hydrogen cyanide through the solution to the pump.
- 5. The Amount of Indicator.—It was found that 1 drop of a 10% solution of potassium iodide per 15 cc. of solution gives accurate results, as checked by other methods.
- 6. The Air Drawn through the Solution.—The atmospheric elements do not interfere with the determination, and the air drawn through the solution, therefore, need not be washed; carbon dioxide serves to facilitate (slightly only) the removal of hydrogen cyanide from the first cylinder. Hydrogen sulfide is the only common impurity of the laboratory that would interfere. When this gas is present in the laboratory, the air should first be passed through a solution of lead nitrate or sodium hydroxide before it is admitted to the cyanide solution.
- 7. Sensitivity of the Method.—It was found very easy to aerate 5 mg. of hydrogen cyanide from 100 cc. of solution and titrate the latter in a 150cc. volume of 5% alkali in the second cylinder. This shows a recovery of 0.00005 g. of hydrogen cyanide per cc. of solution.

This procedure is a highly accurate method for determining simple, soluble cyanides which readily dissociate in solution to produce free hydrogen cyanide when an acid is added. It can be used to determine cyanides in the presence of any impurity, except sulfides, which pass over in the aeration process as hydrogen sulfide and thus interfere with subsequent titration. When sulfides are present, it is necessary to add an excess of lead nitrate to the cyanide solution in Flask A before adding

the acid and aerating. This treatment precipitates the sulfides as lead sulfide and the usual procedure can then be followed.

The Estimation of Mercuric Cyanide

Mercuric cyanide dissociates so little in solution that it does not give a precipitate with silver nitrate. In a pure solution it can be titrated with standard iodine solution (the Fordos and Gelis process). But no method has been developed to determine this substance in the presence of foreign matter, since it defies distillation for quantitative recoveries. A method was, therefore, devised for converting mercuric cyanide into hydrogen cyanide which is then removed by aeration and determined as previously described.

Procedure.—Place 150 cc. of a 5% solution of sodium hydroxide in Cylinder B, and in Cylinder A place a 50mg. sample of mercuric cyanide dissolved in 100 cc. of water and add a few crystals of solid sodium chloride. Close the apparatus tightly and start the pump to aerate slowly. With a pipet introduce into Flask A, through Tube E, 25 cc. of tartaric acid, then 10 cc. of a 5% solution of stannous chloride. A gray to black precipitate of mercurous chloride and metallic mercury appears immediately in the flask, and hydrogen cyanide is evolved and passes over quantitatively into the sodium hydroxide solution in the second flask. Continue aeration at the same speed as described previously for the determination of potassium cyanide for 2 hours, then disconnect and titrate the contents of the second flask with $0.01\ N$ silver nitrate, using $10\ d$ rops of 10% potassium iodide as an indicator. The reading of the buret multiplied by 0.002526 will give the number of g. of mercuric cyanide in the sample.

Description of the Method.—The principle involved here is that mercuric cyanide in solution is reduced to mercurous chloride and metallic mercury in the presence of hydrochloric acid and stannous chloride. The cyanide is liberated as hydrogen cyanide and passes over quantitatively into the second flask when aeration is applied; $2\text{Hg}(\text{CN})_2 + 4\text{HCl} + \text{SnCl}_2 \longrightarrow 4\text{HCN} + 2\text{HgCl} + \text{SnCl}_4$; and $\text{Hg}(\text{CN})_2 + 2\text{HCl} + \text{SnCl}_2 \longrightarrow 2\text{HCN} + \text{Hg} + \text{SnCl}_4$.

A mixture of stannous chloride with hydrochloric acid or with sulfuric acid and sodium chloride, or with tartaric acid and sodium chloride, will give satisfactory results. The author has consistently used tartaric acid as the acidifying agent for reasons previously given. The same principles, as discussed under the potassium cyanide determination, apply to all the other details of procedure for estimating mercuric cyanide.

The methods described above are universal in their application. They can be used to determine simple soluble cyanogen compounds in the presence of practically any other substances. To test their range of application, known amounts of potassium cyanide and of mercuric cyanide

were added to mixtures of blood and organic matter, and quantitative recoveries were obtained by following the procedures as outlined above.

Summary

An aeration procedure for estimating cyanides has been devised in which freed hydrogen cyanide is washed with air into dil. alkali solution, and the mixture then titrated with standard silver nitrate solution, using a little potassium iodide as indicator. The new method has the following marked advantages as compared with the older distillation methods: (1) it avoids loss from hydrolysis of hydrogen cyanide; (2) it can be used to determine cyanides in the presence of ferrocyanides, etc.; (3) it is entirely free from danger to the operator; (4) it offers an excellent method for determining mercuric cyanide provided the latter is previously reduced to mercurous chloride, metallic mercury and hydrogen cyanide with stannous chloride, in the presence of hydrochloric acid; (5) it involves easy technique, gives highly accurate results, and possesses a very wide range of application.

WASHINGTON, D. C.

[Contribution from the Analytical Laboratory, Massachusetts Institute of Technology]

THE REACTION BETWEEN BROMINE AND AMMONIUM SALTS AND ITS EFFECT ON THE PRECIPITATION OF MANGANESE DIOXIDE

By Stephen G. Simpson Received March 26, 1923

One of the standard methods for separating titanium, iron, aluminum and phosphoric acid from bivalent elements such as manganese, magnesium and calcium, is the basic acetate procedure. In the filtrate from this separation, manganese is often precipitated from hot solution by the addition of bromine water: $Mn^{++} + Br_2 + 3H_2O = MnO_2.H_2O + 2Br^- + 4H^{+,1}$ In neutral solution the oxidation and precipitation of the manganese does not take place to an appreciable extent unless the acid formed by the reaction is neutralized, for hot, dil. hydrobromic acid dissolves manganese dioxide. After the basic acetate precipitation, however, the filtrate always contains enough acetate to prevent the formation of an appreciable quantity of free hydrobromic acid, owing to the formation of slightly ionized acetic acid. Sometimes it is the practice to neutralize the solution with dil. ammonia, but owing to the fact that bromine reacts with ammonia $(8NH_4OH + 3Br_2 \longrightarrow 6NH_4^+ + 6Br^- + 8H_2O + N_2)$, a great deal of bromine is used up and it is a rather troublesome operation to precipitate

¹ Compare Wright and Menke, J. Chem. Soc., 37, 22 (1880).

the manganese completely.² When manganese is precipitated from weakly acetic acid solution by bromine, it carries with it elements of the alkali and alkaline-earth group¹ and a single precipitation is not sufficient to effect a complete separation of manganese and these elements, although this method of separation is given in many textbooks. Furthermore, when the solution contains ammonium salts, it is usually difficult in faintly acid solutions to obtain any precipitate of manganese dioxide at all.

The reason why ammonium salts prevent the precipitation of manganese after the basic acetate separation is not generally mentioned in textbooks, and the extent of this interference and the quantitative effects of the several factors involved have been little studied.

Bromine reacts with ammonium salts according to the equation, 2NH₄+ $+3Br_2 \rightarrow 6Br^- + N_2 + 8H^+$, and Ostwald and Raich³ have shown that the velocity of reaction depends upon the strength of the acid forming the negative radical of the ammonium salt. A study of these reactions, moreover, involves a consideration of the reactions between bromine and water. Solutions of bromine contain not only free dissolved bromine, but also hypobromous and hydrobromic acids, Br₂ + H₂O \longrightarrow Br⁻ + HBrO + H⁺, the reaction at 25° using up about 0.8% of the total bromine present.4 Bromine also decomposes water according to the equation $2Br_2 + 2H_2O \rightarrow$ $4Br^{-} + O_{2} + 4H^{+}$, the decomposition increasing rapidly in the sunlight and with increase in temperature.⁵ This latter reaction may be considered simply as a decomposition of the hypobromous acid formed above: 2HBrO \longrightarrow 2H⁺ + 2Br⁻ + O₂. Above 60° bromate is likewise formed:⁶ $3Br_2 + 3H_2O \longrightarrow 5Br^- + BrO_3^- + 6H^+$, or, $3HBrO \longrightarrow BrO_3^- +$ 2Br⁻ + 3H⁺. The various oxidation potentials between these bromine compounds have been determined and the results have been correlated and listed by Abegg.7 The results, however, are found to lie close to one another and likewise close to the oxidation potential between manganous ion and manganese dioxide.8 It is of interest, therefore, to study these reactions experimentally under the conditions where manganese is often precipitated in practice.

Experimental Part

The quantitative effect of the various factors influencing the oxidation of ammonium salts and of manganous salts by bromine was determined experimentally from the amount of bromine used up in each reaction in which

- ² Compare Hall and Williams, "The Examination of Iron, Steel and Brass," McGraw-Hill Book Co., 1921, p. 79.
 - 3 Ostwald and Raich, Z. physik. Chem., 2, 124 (1888).
 - 4 Bray, This Journal, 32, 932 (1910); 33, 1487 (1911).
 - ⁵ Richards and Stull, Z. physik. Chem., 41, 555 (1902).
 - ⁶ See Luther and Sammet, Z. Elektrochem., 11, 293 (1905).
 - ⁷ Abegg, "Handbuch der Anorganischen Chemie," S. Hirzel, 1913, Vol. IV, p. 302.
 - ⁸ Landolt-Börnstein, "Physikalish-Chemische Tabellen," 4th ed., p. 256c.

it takes part. Since the precipitation of manganese dioxide by bromine is usually carried out in hot solution, each determination was made in this way. To do this, use was made of a special 500cc. glass-stoppered distilling flask with the side arm forming the inner tube of a Liebig condenser. The total volume of each solution was 100 cc., and in all determinations the conditions were kept as nearly constant as possible. In each case, after the addition of bromine to the solution, the mixture was allowed to remain quiet in the distilling flask for 5 minutes and then heated to boiling for 10 minutes more, all the free bromine being expelled by the end of this time. The bromine evolved was allowed to pass through the condenser and was caught in potassium iodide solution, the liberated iodine being titrated with standard thiosulfate solution. In this way, when the amount of bromine added and the amount recovered were known, the quantity used up in a reaction was found by difference. The solutions of bromine were standardized repeatedly during each series of distillations, and approximately 1.1 milliequivalents of bromine were used in each reaction, that amount being in each case in excess of the amount theoretically required.

The addition of samples of bromine water to potassium iodide solutions was found to liberate iodine from neutral solutions in amounts corresponding to an average of 98.3% of the total bromine present. After acidification of the solution with sulfuric acid, iodine equivalent to the remaining bromine was liberated. This indicates the presence of oxy-acids of bromine in the solutions used in amounts corresponding to 1.7% of the total bromine present. In any oxidation in acid solution by means of bromine water the presence or intermediate formation of hypobromite or bromate has, however, no quantitative effect, since the oxidizing power expressed in equivalents remains the same. A bromine solution in which a part of the bromine reacts with water to form hypobromite or bromate suffers no loss or gain in oxidizing power.

Ten distillations of samples of bromine water in the apparatus and under the conditions mentioned above showed a net loss in oxidizing power between the original solution and the distillate obtained corresponding to an average of 0.032 + 0.006 milliequivalent of bromine. This represents a 3% decomposition into bromide and oxygen. The residual solution did not oxidize iodide in acid solution.

The initial presence of acid in the distillation of bromine water in 10 similar experiments caused a slight decrease in the loss in oxidizing power of the distillate over the original solution taken, the average loss in terms of bromine being reduced to 0.024 + 0.004 milliequivalent. Since the reaction by which hypobromous acid is formed from bromine and water is reversible, the initial presence of acid, by its common ion effect, reverses the reaction and hence retards the loss in oxidizing power caused by decomposition of hypobromite into oxygen and bromide.

In the experimental study of the reaction between bromine and ammonium salt, the sulfate of ammonium was used because of the fact that it reacts with bromine moderately rapidly, being intermediate between the chloride or nitrate and the acetate. The amount of bromine used up in each reaction was determined by means of the apparatus and under the conditions described above. In the absence of sodium acetate and with a large excess of bromine, the reaction between ammonium ion and bromine

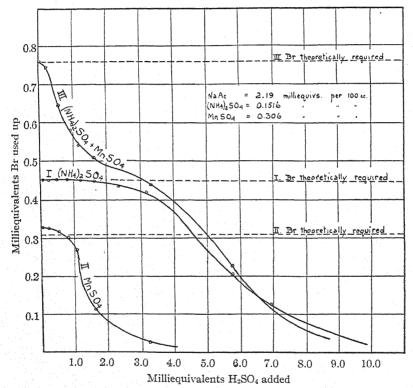


Fig. 1.—Consumption of bromine by boiling for 10 minutes with (I) (NH₄)₂SO₄; (II) MnSO₄; (III) (NH₄)₂SO₄ + MnSO₄ in various concentrations of acid

was found to take place quantitatively according to the reaction, $3Br_2 + 2NH_4^+ \longrightarrow 6Br^- + N_2 + 8H^+$, but the reaction is moderately slow, so that with comparatively great amounts of ammonium sulfate the time of contact with the bromine water was not sufficient to cause the oxidation of all the ammonium salt, for the bromine was expelled before the oxidation was complete. The presence of increasing amounts of acid in the original solutions, on the other hand, caused a corresponding retardation of the reaction and the presence of a moderately high concentration of hydrogen ion was capable of stopping the reaction practically completely.

The extent of the oxidation of ammonium ion by bromine in the presence of sodium acetate under varying concentration of acid and under the experimental conditions is shown in Fig. 1 (I). With a moderate excess of acetate it is seen that the theoretical amount of bromine required for the ammonium salt is consumed. Only when the concentration of acid exceeds that of the acetate is the reaction retarded, and to a degree which increases with the excess of acid present.

The explanation of these phenomena follows from a consideration of the fact that although the reaction $3\mathrm{Br_2} + 2\mathrm{NH_4}^+ \longrightarrow 6\mathrm{Br}^- + \mathrm{N_2} + 8\mathrm{H}^+$ is in itself practically irreversible, the reaction $\mathrm{Br_2} + \mathrm{H_2O} \Longrightarrow \mathrm{Br}^- + \mathrm{HBrO} + \mathrm{H}^+$ is distinctly reversible, and it is the hypobromous acid formed that causes rapid oxidation of ammonium ion: 9 $2\mathrm{NH_4}^+ + 3\mathrm{HBrO} \longrightarrow \mathrm{N_2} + 3\mathrm{Br}^- + 3\mathrm{H_2O} + 5\mathrm{H}^+$. The initial presence of acid, by reversing the equilibrium reaction between bromine and water and hence lowering the concentration of hypobromite, retards the oxidation of ammonium ion. Conversely, the presence of acetate, by removing hydrogen ion in the form of relatively non-ionized acetic acid, causes the equilibrium reaction as written above to proceed to the right and thereby accelerates the oxidation of ammonium ion by the hypobromous acid formed.

Experiments in which a great excess of sodium acetate over the acid initially present was used, showed a consumption of bromine slightly greater than the amount theoretically required for the ammonium alone. The hypobromous acid, in this case being formed in comparatively large amounts, after oxidizing the ammonium ions present, decomposes appreciably into oxygen and hydrobromic acid, and hence causes a corresponding loss in oxidizing power.

In the study of the oxidation of manganese by bromine, the sulfate of manganese was used and the reactions were carried out in the apparatus and under the same conditions as in the oxidation of the ammonium salt. The values obtained are expressed graphically in Fig. 1 (II). Without the presence of alkali acetate, the oxidation of manganese by bromine takes place to a very slight degree; with sodium acetate present in excess, manganous ion is completely oxidized and precipitated by bromine water, provided no acid is originally present in the solution. An increase in the initial concentration of acid causes a marked decrease in the extent of the reaction, and the effect, be it noted, is much greater than in the case of the ammonium salt oxidation.

These reactions can be explained in exactly the same way as was the oxidation of ammonium ion, for although the reaction, $\mathrm{Mn^{++}} + \mathrm{Br_2} + 3\mathrm{H_2O} = \mathrm{MnO_2}, \mathrm{H_2O} + 2\mathrm{Br^-} + 4\mathrm{H^+},$ is in itself reversible, yet the same oxidation may be expressed through the hypobromous acid formed as a product of the equilibrium reaction between bromine and water: $\mathrm{Mn^{++}} +$

Compare Bray and Livingston, This Journal, 45, 1251 (1923).

 ${\rm HBrO} + 2{\rm H}_2{\rm O} = {\rm MnO}_2.{\rm H}_2{\rm O} + {\rm Br}^- + 3{\rm H}^+.$ As with the ammonium-ion oxidation, the initial presence of acid or accetate affects the hypobromite equilibrium sufficiently to retard or accelerate the manganese precipitation. With small amounts of acid, the quantity of bromine used up is seen from the graph to be in excess of the amount theoretically required for the manganese alone, due, as in the case of the ammonium salt reaction, to decomposition of the hypobromous acid into oxygen. Increasing the acetate concentration, even when a moderate concentration of acid had been added, caused increased precipitation of manganese dioxide, but also caused increased loss in oxidizing bromine.

The conditions resulting when bromine reacts with solutions containing both manganous ions and ammonium ions are shown in Fig. 1 (III), where the same experimental conditions were maintained as in the individual reactions. These experiments show that with sodium acetate present, but with little or no acid initially present, the amount of bromine used up is approximately equal to the sum of the theoretical amounts calculated for the manganese salt and for the ammonium salt. Increasing acid concentration, however, rapidly reduces the bromine consumption to a point where both reactions practically cease. Comparison with the individual effects of manganese sulfate and ammonium sulfate shows that under the experimental conditions, when manganous ion and ammonium ion are present together, the addition of bromine causes more rapid oxidation of the ammonium ion than of the manganous ion.

The extent of precipitation of manganese dioxide in the presence of various amounts of ammonium sulfate was next determined using an excess of sodium acetate and a great excess of bromine water. No acid was added, and 0.302 milliequivalent of manganese was employed in each case. After the solution had been boiled, the precipitated manganese dioxide was determined by titration. The results obtained are given below, and from them it is seen that a moderate concentration of ammonium ion inhibits to a marked degree the precipitation of manganese dioxide.

(NH4)2SO4 added Millieq.	Mn pptd. Millieq.	Mn pptd.	(NH ₄) ₂ SO ₄ added Millieq.	Mn pptd. Millieq.	Mn pptd. %
0.000	0.301	100	0.303	0.267	87
.030	.303	100	.394	.170	56
.091	.302	100	.606	.008	1.4
.152	.289	95	.909	.004	0.7
.243	.280	91			

Conclusions

In the precipitation of manganese by oxidation with bromine water to manganese dioxide in hot solution, the presence of ammonium salts has a decidedly inhibiting effect. The extent of the effect depends principally upon three similar reactions, as follows:

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2Br_2 + 2H_2O = 4Br^- + O_2 + 4H^+

3Br_2 + 2NH_4^+ = 6Br^- + N_2 + 8H^+

Br_2 + Mn^{++} + 3H_2O = 2Br^- + MnO_2H_2O + 4H^+
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Each of these reactions may be expressed through the intermediate formation of hypobromous acid according to the equilibrium: $Br_2 + H_2O \rightleftharpoons Br^- + HBrO + H^+$, and the subsequent oxidation of the reducing agent in question by the hypobromous acid thus formed, the hypobromous acid reacting more rapidly with the reducing agents than does bromine itself. The initial presence of acid by its common ion effect, and the presence of alkali acetate by its ability to cut down the hydrogen-ion concentration, disturb the above equilibrium reaction, causing marked variation in the hypobromite concentration and hence retard or accelerate the oxidation reactions, as the case may be.

In hot solution and in the presence of alkali acetate, bromine water oxidizes ammonium ion more readily than it does manganous ion. With no acid initially present and with a moderate excess of acetate, ammonium ion is quantitatively oxidized by an excess of bromine. After this oxidation is complete, the presence of large amounts of acetate causes consumption of any excess bromine present, due to the decomposition of hypobromous acid into bromide and oxygen with corresponding loss in oxidizing power. Without the presence of acetate, ammonium salts are likewise oxidized quantitatively by bromine water in neutral solution, but the reaction proceeds much more slowly, and the rate of reaction varies inversely with the ionization of the acid forming the negative radical of the ammonium salt.

The precipitation of manganese by bromine water in hot, neutral solution is almost inappreciable in the absence of acetate. With alkali acetate present, in neutral solution manganese is quantitatively oxidized and precipitated from solution on boiling with excess bromine. The extent of precipitation is greatly influenced by the initial acidity of the solution, more so than in the ammonium salt reaction. A large excess of sodium acetate makes the precipitation of manganese dioxide more complete, but causes excessive consumption of bromine by its decomposition of water which occurs almost simultaneously. Manganese dioxide can be precipitated quantitatively from neutral solution in the presence of a slight amount of ammonium salts when sodium acetate is present in excess, and in such a case both the ammonium salt and the manganese salt are completely oxidized. With an increase in the concentration of the ammonium salt, the precipitation of the dioxide is retarded, and with a moderate excess of ammonium salt can be almost entirely prevented. The ammonium salt, being oxidized more rapidly, forms by its reaction a sufficient concentration of hydrogen ion to prevent the manganese precipitation.

When manganese is to be precipitated as dioxide after a basic acetate separation, it is important, therefore, that no appreciable amounts of ammonium salts are present. If present, they should be removed previous to the precipitation by evaporation with aqua regia. It sometimes happens that in the evaporation of the filtrate from a basic acetate separation, a small precipitate results which may be (1) manganese dioxide due to oxidation of the manganese by the air; or (2) more basic acetate of a tervalent element due to incomplete basic acetate separation; or (3) a mixture of the two. In such a case, the precipitate should either be put through another basic acetate procedure, or it may be dissolved in acid and the tervalent element precipitated by ammonium hydroxide in the presence of ammonium salt10 and removed by filtration. In the latter case, the filtrate containing any possible manganese should not be added to the main filtrate. since it now contains ammonium salts and would prevent the subsequent precipitation of manganese dioxide. This auxiliary filtrate should, therefore, be saved and added to the main solution after the manganese dioxide has been precipitated, redissolved, and is ready for precipitation as manganese ammonium phosphate.

Summary

- (1) The effect of the presence of ammonium salt on the precipitation of manganese dioxide by bromine water following a basic acetate separation was studied by determining the amounts of bromine used up in reactions with solutions of (a) ammonium sulfate, (b) manganous sulfate, (c) mixtures of the two, under varying degrees of initial acidity and in the presence of varying amounts of alkali acetate. The numerical values obtained are graphically tabulated for comparison.
- (2) The tabulated results show that each of the reactions is progressively retarded by an increase in the initial concentration of acid, and progressively accelerated by an increase in the concentration of acetate present, and the effect is greater in the case of the manganese salt than in the corresponding case of the ammonium salt.
- (3) In the absence of acid, ammonium ion and manganous ion are quantitatively oxidized by bromine water, but the amount of free bromine used up is slightly in excess of the amount theoretically required.
- (4) The results obtained can be explained by considering the mass-action effect of hydrogen ion and of acetate ion on the equilibrium reaction between bromine and water, and assuming that the hypobromous acid formed oxidizes ammonium ion and manganous ion more readily than does bromine, and under the existing conditions also decomposes slightly into oxygen and bromide.
- (5) When ammonium salts and manganese salts are present together in neutral solution in the presence of acetate, the ammonium ion is more ¹⁰ See Lundell and Knowles, This Journal, **45**, 676 (1923).

readily oxidized by bromine water, and by its formation of hydrogen ion retards the precipitation of manganese dioxide.

Cambridge 39, Massachusetts

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PARTIAL AND CONSECUTIVE REACTIONS IN THE PHOTO-SENSITIVE SYSTEM: QUININE SULFATE, CHROMIC AND SULFURIC ACIDS

By George S. Forbes, John C. Woodhouse and Reginald S. Dean Received April 21, 1923

The general photochemical equation of Plotnikow¹ provides for reactions involving more than one photosensitive substance, and also "dark" reactants indispensable but not activated under the given conditions

$$-dM/dt = KA_1A_2...A_n(a-x)^{n_1}(b-x)^{n_2}...(p-x)^{n_n}$$

where A_1 and A_2 are the rates of light absorption by Reactants 1 and 2, to which the concentrations of their activated molecules C_1' and C_2' are approximately proportional, while (a-x), (b-x) are concentrations of "dark" reactants. The reaction between these molecular species, determined by these concentrations, has a velocity constant k_1 .

The photochemical oxidation of quinine by chromic acid in the presence of sulfuric acid was investigated in 1906-7 by Luther and Forbes.²

The first two reactants are known to be photosensitive in various reactions; the third is undoubtedly a dark reactant. The data of this research should, therefore, serve to test Plotnikow's equation. When the test is made, however, it is found that chromic acid seems to behave only as an inert light filter, and that the reaction velocity is independent, within the limit of error, of the light absorbed by it, and not proportional to the latter, as Plotnikow's equation requires. Plotnikow's is of the opinion that some experimental error or inadequate analysis of the data on absorption is responsible for the discrepancy. We desire first to show deductively that in a system containing 2 photosensitive reactants capable of reacting even in the dark, there are doubtless partial reactions not provided for in Plotnikow's equation. The discrepancy may be explained in terms of these. Also, with the help of new experimental data, we shall thereafter demonstrate the limitations inherent in that factor of Plotnikow's equation which deals with the dark reactant.

Let the concentrations of unactivated molecules of 2 photosensitive reactants be C_1 and C_2 . In the dark, $-dM/dt = k_2C_1^{\ p}C_2^{\ q}(a-x)^{n_1}$... and k_2 may be evaluated. During illumination, according to the usual

¹ Plotnikow, "Allgemeine Photochemie," Vereinigung Wissenschaftlicher Verleger, 1920, p. 185.

² Luther and Forbes, This Journal, 31, 770 (1909).

³ Ref. 1, pp. 215, 416, 583.

assumptions, C_1 and C_2 are still large compared with C_1' and C_2' , and k_2 still applies to these unactivated portions. Then the contribution to the total reaction velocity in the illuminated system made by C_1 and C_2 is calculated from k_2 and the *total* concentrations of the reactants. This contribution is usually subtracted from the total reaction velocity in light to find -dM/dt, the photochemical reaction velocity proper, due to C_1' and C_2' . Obviously, the general equation anticipates these two and only these two reaction types.

But two other partial reactions, not provided for by previous investigators, now appear inevitable. For if the unactivated C_2 reacts with unactivated C_1 and (a-x), it can scarcely escape reaction with the activated C_1' and (a-x), introducing the velocity constant k_3 , where $k_1 > k_3 > k_2$. Likewise C_1 will react with C_2' and (a-x), introducing a fourth constant k_4 , where $k_1 > k_4 > k_2$. The greatest divergences from Plotnikow's equation should now occur if C_1' and C_2' are both relatively small, and k_3 , for instance, is almost as great as k_1 while k_4 is but little greater than k_2 . The experimenter would then conclude that -dM/dt was closely proportional to A_1 , and practically independent of A_2 . If now we write quinine as Reactant 1 and chromic acid as Reactant 2 in the above picture, we have at once a rational explanation of the anomaly which led Plotnikow to object to the conclusions of Luther and Forbes.

Such a mechanism virtually assigns to chromic acid the role of a dark reactant, to whose concentration or some power of the same the reaction velocity should perhaps be proportional. But Luther and Forbes found no such relation, except when C_2 was small compared with C_1 , and A_1 was relatively large. They explained this in terms of two consecutive reactions, the first involving activation of quinine, the second actual oxidation by chromic acid. When C_2 fell below 0.0005, C_1 was not, by oxidation, diminished much below the constant stationary value C_1 which it could have attained under conditions the same except for complete absence of chromic acid. Then -dM/dt should be closely proportional to C_2 , as Luther and Forbes observed. But when C_2 was large, and especially when a-x was large also, C_1 was at all times much less than C_1 ". One would now expect that changes in C_2 would be relatively unimportant, but that C_1 and A_1 would practically determine reaction velocity, as was also proved.

But it was the influence of the dark reactant proper (sulfuric acid in this case) that chiefly interested us. According to Plotnikow's equation the reaction velocity should be in all cases proportional to some constant power one, for instance of the concentration of such a dark reactant. The previous data bearing on this problem are scanty. Most workers on photochemistry, Luther and Forbes among them, have evaded it by keep-

⁴ Plotnikow, Z. physik. Chem., 58, 219 (1907).

ing a-x both large and unvaried. Some, like Chapman,⁵ in his work on the chlorine-hydrogen reaction, mentions the minimum concentration which is without influence on reaction velocity. We know of no adequate experimental study of such questions.

Materials.—v. s. p. Quinine sulfate, thrice recrystallized and dried over sulfuric acid, melted at 204.6° . The potassium dichromate was recrystallized and dried at 110° before weighing out. Standard sodium thiosulfate solutions made up from thrice recrystallized salt a month before the work began gave titers of 0.01091 and 0.02285 against dichromate.

The light source was a Cooper-Hewitt quartz mercury lamp, type designed for 110 volts and 4 amperes. Owing to the well-known inconstancy of such lamps, each new reaction mixture was exposed to light side by side with a reference solution in which the initial concentrations were invariably: $C_1 = 3$ g./liter, $C_2 = 0.010$ g. equivalent (0.0033 mole) per liter, a = 0.977 g. equivalent per liter.

The reaction vessel was a 95mm, crystallizing dish divided into semicircular segments by a vertical partition. We proved by special experiments that typical reaction mixtures maintained their titer unchanged for a long time in contact with considerable surfaces of the de Khotinsky cement used. The 95mm. dish was placed inside a 140mm. dish on ledges several millimeters high, and surrounded by water and ice frequently renewed. The temperature variations were unimportant. The combination was mounted on a pivoted wooden disk which, by means of a geared-down electric motor and an eccentric, was made to turn back and forth through an angle of 150° a dozen times per minute. Glass grids dragging through the solutions in the inner dish kept them well stirred. The lamp was fastened in a position always the same with respect to the reaction vessel, about 10 cm. above it. As the segments were not exactly equal in area, or in illumination received, experiments were made at intervals with identical solutions in both segments. The ratio between the quantities of chromic acid reduced was used as a factor to correct the ratios found in the regular experiments. The time of exposure to light was planned, as closely as possible, to reduce about 10% of the reference solution, and it was then assumed that the corrected ratio between the quantities of chromic acid reduced represented nearly enough the ratio between total reaction velocities at the start of the given experiment.

In each experiment a third solution, identical with the new reaction mixture, was made up simultaneously, left in the dark during the run, and then titrated under strictly parallel conditions. Less frequently the dark reaction of the reference solution was checked. Upon subtraction, $-\mathrm{d}M/\mathrm{d}t$ resulted with elimination of systematic titration errors.

Iodimetry was adopted in spite of well recognized uncertainties, some of which have since been cleared up.⁶ The contents of reaction vessels, with rinsings, were transferred to conical flasks. Oxygen was excluded by a stream of carbon dioxide. Equal quantities of water were added, and of acid also, except when the original solutions contained a sufficient excess. The iodine set free when excess of iodide was added was at once discharged by standard thiosulfate solution, adding the starch at the end. The flasks, sealed for half an hour were again titrated, and once more after an additional 2 hours, if necessary. Thus the liberation of iodine, very

⁵ Chapman and Whiston, J. Chem. Soc., 115, 1267 (1919).

⁶ Vosburgh, This Journal, 44, 2120 (1922).

slow in presence of very dilute chromic acid, became complete without error from atmospheric oxygen.

Weigert and Saveanu⁷ have investigated the photochemical oxidation of quinine by atmospheric oxygen. Fearing that this might complicate the oxidation by chromic acid, we repeated typical experiments previously made in air, surrounding the reaction vessel with a tall cylinder kept full of carbon dioxide from a tank. Actual analyses gave 70% to 90% by volume. The results were unchanged, within the limit of error.

With acid concentrations not greater than $0.02\,N$ the quantities of acid consumed during illumination were estimated through preliminary experiments, and enough $0.5\,N$ acid was gradually added to keep its concentration nearly constant.

Data and calculation of a typical experiment follow.

Solution 1: Segment I, 0.15 g. of quinine, 0.0245 g. of potassium dichromate, 0.0239 g. of sulfuric acid, volume, 50 cc. Then $C_1 = 3$ g. per liter, $C_2 = 0.01$ equivalent normal, a = 0.977 equivalent normal. Solution 2: volume 50 cc., Segment II, $C_1 = 3$ g. per liter; $C_2 = 0.01$, a = 0.106. Dark solutions 3 and 4, identical with 1 and 2.

Titers after 2 hours at 0°, nearly: (1) = 42.65 cc. of sodium thiosulfate, (3) = 46.85 cc.; $-\Delta C_2 = 4.20$. (2) = 43.20 cc., (4) = 46.48 cc.; $-\Delta C_2 = 3.28$.

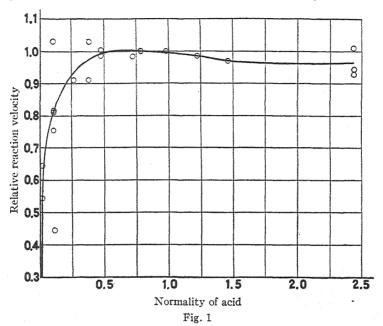
Ratio corrected for inequality of segments = $3.28/4.20 \times 0.971 = 0.78$.

Let us first predict the effect of changing chromic acid concentration, C_1 and a being constant. In the present research A_1 was much greater than in the work of Luther and Forbes through substitution of a quartz lamp for one of uviol glass, and by eliminating 2 layers of common glass between lamp and solution. This fact, and our lower acid concentrations, should make the order of reaction with respect to chromic acid increase beyond zero before its concentration fell below $0.0005\ N$. This point is reserved for later investigation.

As the experimental conditions were not reproducible, complete data are not given. The results, where C_2 was constant, are presented simply by plotting against acid concentrations the ratios of reaction velocities in various solutions to that in $0.977\ N$ acid under conditions otherwise the same. Above $0.5\ N$, velocity is nearly independent of acid concentration. No explanation for the slight but unmistakable maximum could be found. Perhaps there is an increased absorption in this region. Below $0.5\ N$ the order of reaction with respect to acid rapidly increases. Between $0.02\ N$ and $0.01\ N$ it is 1, and at lower concentrations it presumably tends toward 2, the order in the dark which we established by special experiments over long periods. Insoluble precipitates, forming when a < 0.01, discouraged investigations in such solutions. It is clear, however, that photochemical reaction velocity could be proportional to the expected power of this dark reactant only at very low concentrations of the latter. Here the actual rate of oxidation of the quinine is slow in comparison with

Weigert and Saveanu, Nernst-Festschrift, 1912, 464.

its speed of activation, and determines the total reaction speed. In this region, and in this region only, Plotnikow's generalization as to the dark reactant is applicable. On the other hand, it would apply over the widest ranges of concentration, in reactions where the velocity of the reaction



stage involving the dark reactant was always small in comparison with the speed of activation.

We gratefully acknowledge a grant from the Cyrus M. Warren Fund for the purchase of a quartz lamp, and a grant from the Du Pont Fund.

Summary

With 2 photochemically activated reactants the total reaction velocity should be the sum of 4 partial reactions with 4 different velocity constants. One involves 2 activated molecular species, another only unactivated species, and 2 others involve 1 activated and 1 unactivated species. It is shown how species known to be activated in some reactions may give no evidence of activation in others.

The concentration of a photochemically unactivated reactant is shown to be without effect upon the velocity of a photochemical reaction provided that its concentration is not so small that its reaction with activated reactants does not become the slow stage of the total process.

CAMBRIDGE 38. MASSACHUSETTS

[Contribution from the Havemeyer Chemical Laboratory, New York University]

THE INFLUENCE OF NEUTRAL SALTS ON THE TEMPERATURE COEFFICIENT OF REACTION VELOCITY

By F. O. RICE AND WILLIAM LEMKIN¹
Received May 9, 1923

The reaction we studied is that between acetone and iodine in dilute aqueous solution, and our technique and methods are described in a previous paper. The velocity constant used throughout this paper is the (calculated) number of moles of iodine disappearing per minute from 1 liter of a solution containing 1 mole of acetone, 1 gram equivalent of acid, about $0.01\ N$ iodine, and a stated amount of neutral salt. The solution also contained $0.025\ M$ potassium iodide to keep the iodine in solution. When this constant was determined at two temperatures for a solution of the same composition, the ratio is referred to as the temperature coefficient of the reaction. We are thus comparing the velocities at two temperatures for solutions containing the same concentration of total acid.

Lamble and Lewis³ have attempted to calculate the temperature coefficient for solutions of equal hydrogen-ion concentration. Since, in the case of our solutions, there are no reliable data for making the necessary calculations, and there is not even agreement as to the nature of the catalyst,⁴ we have not attempted to calculate the temperature coefficient for equal concentrations of catalyst.

The abnormal action of neutral salts is commonly ascribed to hydration effects and therefore, we made a preliminary study of the effect of lithium nitrate on the velocity and temperature coefficient of the reaction. We selected this salt because it shows very abnormal changes in solubility over the temperature range 20–30°. The solubility of lithium nitrate is almost doubled between 23° and 30°, and the salt also possesses a congruent melting point and a transition point, $3\rm{H}_2\rm{O}-1/2\rm{H}_2\rm{O}$, between these two temperatures. In previous investigations the salts used showed normal changes in solubility over the region investigated and we hoped, therefore, to find the velocity measurement affected by the abnormal hydration effects.

We crystallized the lithium nitrate twice from distilled water, and by a blank test showed that a 2N solution of the salt absorbed no appreciable amount of iodine over a period of 4 hours. We also tested to see whether

¹ The work included in this paper is summarized from the thesis presented by William Lemkin, submitted as part of the requirement for the degree of Doctor of Philosophy in New York University.

² Rice and Kilpatrick, This Journal, 45, 1401 (1923).

² Lamble and Lewis, J. Chem. Soc., 105, 2330 (1914).

⁴ Kendall, Proc. Nat. Acad. Sci., 7, 56 (1921).

lithium nitrate alone had any catalytic activity. The results in Table I show that the neutral salt alone has no measurable catalytic action.

Table I

Effect of Lithium Nitrate on the Reaction, CH₃COCH₃ + I₂

Concentration of acetone, 0.071 (M)

Concentration of acceptate, 0.071 (m)							
Salt present	None	None	$2.2~M~{ m LiNO_3}$	2.2 M LiNO3			
N iodine, initial	0.01162	0.01162	0.01050	0.01050			
After 300 min	0.01161	0.01161	0.01047	0.01049			

For the velocity measurement we used nitric acid as catalyst. By passing air through the acid for several hours we removed all traces of oxides of nitrogen, which would decompose the hydriodic acid formed during the reaction. Table II gives the results of our measurements at 23° and 30° with and without lithium nitrate.

Table II $\begin{tabular}{ll} Velocity Constants with and without Lithium Nitrate at 23° and 30° \end{tabular}$

,-,-			.,			
Temp.	Constant per liter	Av.		Temp.	Constant per liter	Av.
N	To salt present			2.102	$2~M~{ m LiNO_3}$ pres	sent
23.00	13.58			23.00	20.13	20.12
	13.60	13.58			20.11	
	13.56			23.00	20.09	20.05
23.00	13.62				20.02	
	13.59	13.58			20.05	
	13.55					
				2.103	M LiNO2 pres	ent
30.00	30.49	30.48		30.00	45.06	44.98
	30.48				44.91	
30.00	30.44			30.00	44.98	45.00
	30.30	30.35			45.03	
	30.32					

With no salt present. $k_{30}/k_{23} = 2.2393$, precision measure = 0.20%.

With 2.10 M LiNO₃ present $k_{20}/k_{23} = 2.2401$, precision measure = 0.20%.

The precision measure of a single experiment was taken to be 0.20%.

These solutions all contained about 0.1 $\it M$ acetone, 0.1 $\it N$ HNOs, 0.01 $\it N$ iodine and 0.025 $\it M$ KI.

The result shown in Table II was entirely unexpected because, on the basis of the radiation theory, the great increase in the velocity should be accompanied by a smaller temperature coefficient. Our next step was to investigate whether this behavior was shown by other salts.

Effect of the Neutral Salts of Strong Acids on the Temperature Coefficient

We selected 23° and 25° as the two temperature limits, and measured the temperature coefficient by the method already described which did not involve the measurement of the two velocity constants separately. However, in several cases we measured the velocity constants at the two

temperatures and showed that the temperature coefficients, obtained in this manner, checked with those obtained by the shorter method. The neutral salts used were the highest grades that could be purchased, and in all cases were tested for absorption of iodine. Only those specimens that gave a negligible absorption over the period of an experiment were used. Table III contains the ratios obtained for 6 strong acids alone and in presence of various neutral salts.

 $\label{thm:complex} Table~III \\ Temperature~Coefficients~of~the~Reaction,~CH_3COCH_3~+~I_2,~when~Catalyzed~\\ \text{by Various~Strong~Acids~Alone~and~in~the~Presence~of~Neutral~Salts}$

Acid used	k_{25}/k_{23}	Acid used	Neutral salt M	k_{25}/k_{23}
HNO_3	$\begin{cases} 1.2650 \\ 1.2623 \end{cases}$	HNO3 HCl	2.0 NaCl 1.0 NaCl	1.2625 1.2624
HC1	1.2623	HNO_3	2.0 KNO ₃	1.2634
HI	1.2610	HNO_3	$1.0 \text{ Mg}(\text{NO}_3)_2$	1.2624
HClO ₄	$\int 1.2645$	HC104	1.0 LiClO ₄	1.2610
HClO4	1.2610	HNO_3	3.5 NaCl	1.2630
Benzenesulfonic	1.2613	HNO_3	2.1 LiNO ₃	1.2670
Trichloro-acetic	1.2581	HNO_3	1.81 KNO ₃	1.2642
β -Naphthalenesulfonic	1.2594		Mean	1 = 1.2632
Mean	n = 1.2617			

The acids were present at a concentration about 0.1 N. 0.025 M KI was present to keep the iodine in solution. The precision measure of each experiment is 0.20%.

From Table III we see that the reaction has the same temperature coefficient when catalyzed by strong monobasic acids, and the temperature coefficient is unaffected by the presence of the salts of these acids. In one of our experiments with nitric acid as catalyst we had the solution saturated with sodium chloride and also some of the solid salt present. The temperature coefficient was the same as when no salt was present.

Effect of Moderately Strong Acids and Weak Acids on the Temperature Coefficient, in both the Presence and the Absence of Their Salts

We investigated first the temperature coefficient of the reaction using sulfuric acid alone and in the presence of various concentrations of sodium sulfate. In these cases we measured the velocities of the reactions. The results are given in Table IV.

It will be readily seen from Table IV that the presence of $0.434\ M$ sodium sulfate hardly affects the velocity, yet the temperature coefficient is greatly diminished. In another experiment using less sodium sulfate we found that both the velocity and the temperature coefficient were lowered, which is the opposite of the effect predicted by the radiation theory.

In Table V we give the results for the other acids that we investigated. In the cases of the very weak acids the results are probably slightly higher

TABLE IV

VELOCITY CONSTANTS OF THE REACTION, CH₃COCH₃ + I₂, WHEN CATALYZED BY SULFURIC ACID ALONE AND IN THE PRESENCE OF SODIUM SULFATE

Salt present	None	None 0	434 M NacS	O ₄ 0.434 M	0.87 M	$0.87\ M$	
Temp., ° C		25	23	25	23	25	
Av	12.52	15.56	12.98	15.87	15.56	18.93	
For H ₂ SO ₄ , no sait	present.	k_2	$k_{23} = 1.3$	2430; henc	e Q = 19,	070.	
0.434 M Na ₂ SO ₄ p:	resent.	k_2	$_{5}/k_{20} = 1.3$	2225; henc	eQ = 17	610.	
0.87 M Na ₂ SO ₄ pre	esent.	k _o	$s/k_{00} = 1$	2169: henc	$e \hat{O} = 17$	010	

The precision measure of each experiment is 0.20%, so that the precision measure of k_{25}/k_{23} is 0.28% and the precision measure of Q is 1.2%. For strong monobasic acids Q = 20.540.

Q was calculated from the Arrhenius formula as in the previous paper.2

than the true values, because the hydriodic acid liberated in the reaction probably took part in the catalytic action, and this would tend to raise the temperature coefficient slightly.

TABLE V

Temperature Coefficients of the Reaction, CH₃COCH₃ + I₂, when Catalyzed by Moderately Strong Acids and Weak Acids

Acid	Oxalic	Sulfuric	Phosphoric	Acetic
k_{25}/k_{23}	1.2509	1.2435	1.2410	1.2395
Q	19,630	19,110	18,930	18,820
The precision measure of ker/	$k_{\rm ex} = 0.20\%$	and that of	0 = 0.87%	

Effect of Small Quantities of Neutral Salts on the Velocity of Reaction

We investigated the effect of adding small quantities of neutral salts, especially those salts of the higher alkali metals which are not so extensively hydrated as lithium and sodium salts. We first tried the effect of rubidium nitrate on the reaction catalyzed by nitric acid. There was a distinct increase in the velocity. We then determined to try the effect of still smaller concentrations of salt. It must be remembered however, that in all our experiments it was necessary to have present $0.025\ N$ potassium iodide in order to keep the iodine in solution. By using hydriodic acid as the catalyst we avoided the necessity of having potassium iodide present since iodine is soluble in aqueous hydriodic acid.

We therefore measured the velocity, with hydriodic acid as catalyst and with no neutral salt whatsoever present, and then measured the velocity again after the addition of small quantities of various neutral salts. We did these experiments in pairs, each pair being performed simultaneously in the same thermostat under similar conditions. The absolute velocities were not measured but the conditions were such that we obtained the relative velocities with a high degree of precision. In no case did we detect any fall in velocity due to the addition of neutral salt. If hydriodic acid was 95% dissociated, the addition of $0.01\ N$ neutral salt should diminish the hydrogen-ion concentration about 0.5%, assuming

that the simple mass-action law holds. These results, therefore, in conjunction with the temperature-coefficient measurements give some support to the complete dissociation theory for strong acids.

A theoretical discussion of the results obtained in the paper will be given in a succeeding communication.

TABLE VI

Effect of Very Small Concentrations of Neutral Salt on Velocity of Reaction

Conen. M	0.079	0.053	0.01	0.01	0.01	0.01	0.1
Salt	$RbNO_3$	RbNO ₃	KNO_3	KI	KI	CsNO ₃	$CsNO_3$
Catalyst	HNO_3	HNO_3	$\mathrm{HNO_3}^a$	$_{ m HI}$	HI	HI	HI
% incr. in V	1.9	9.1	2.7	0.16	0.10	0.32	3.0

In the two experiments with RbNO3, 0.025 M KI was present to keep the iodine in solution. This was omitted in all the other experiments.

^a In 30% C₂H₅OH.

Summary

- 1. We have measured the temperature coefficient of the reaction, $CH_3COCH_3 + I_2 = CH_3COCH_2I + HI$, when catalyzed by various acids alone and in presence of their salts.
- 2. The temperature coefficient of all strong acids is the same, and is unaffected by the presence of their salts.
- 3. The reaction has a lower temperature coefficient when catalyzed by weak acids. If the acids are arranged in descending order of their strengths this is also the order of diminishing temperature coefficients.
- 4. When the reaction is catalyzed by sulfuric acid the presence of one of its salts diminishes the temperature coefficient considerably. This is probably true for all weak acids.
- 5. Small quantities (about 0.01 M) of salts of the alkali metals increase the velocity slightly. There is no indication of any diminution such as we might expect on the basis of the mass-action law.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF APPLIED CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A CORRECTION TO THE FREEZING-POINT DIAGRAM OF LEAD-SODIUM ALLOYS

By G. Calingaert and W. J. Boesch Received June 16, 1923

The compounds capable of existing in lead-sodium alloys, as found in the literature¹ are: Na₄Pb, Na₂Pb, NaPb and Na₂Pb₅, and were identified by Mathewson as corresponding to the maxima of the freezing-point diagram of these alloys.

The thermal data obtained by one of the authors of this paper for lead-sodium alloys of approximately the composition, Na₂Pb (66.6 atomic per cent. of sodium), differed appreciably from the results reported by Mathewson. The freezing-point data were therefore determined for alloys between 50 and 75 atomic per cent. of sodium.

Experimental Procedure

The cooling curves were determined on about 100g. samples of each alloy, using a nickel crucible, an iron agitator and a well-lagged electric furnace. In order to prevent oxidation, a slow current of hydrogen was passed through the furnace during all the experiments. The temperature was read at 30- or 60-second intervals by means of a calibrated chromelalumel thermocouple, using a Leeds and Northrup potentiometer. The thermocouple was protected from the corrosive action of the alloys by a Pyrex glass tube, which was but slightly attacked by the sodium.

The lead used was pure, as indicated both by analysis and melting-point determination. The sodium was melted and cut under paraffin oil to free it from hydroxide, and to prevent oxidation. The composition of the alloys was determined by analysis. It was found that the analytical method used by previous experimenters, namely decomposition of the alloy by water, and titration of the sodium hydroxide formed, invariably gave low results, due to incomplete decomposition of the alloy. Accurate analyses were obtained by decomposing the alloy with water, dissolving the residue in nitric acid and then converting both metals into sulfates. After separation from the lead, the sodium was determined gravimetrically as sulfate.

Results

The results are summarized in Table I and plotted in Fig. 1. Fig. 2 is a complete phase diagram of lead-sodium alloys, as given by Mathewson, but corrected according to the work of the authors for the alloys of com-

¹ Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Julius Springer, Berlin, 1912, p. 688. Mathewson, Z. anorg. Chem., 50, 172 (1906).

TABLE I
RESULTS FROM COOLING CURVES

	% by wt.	Atomic %	Temp. o	f		Second in coo	ling
% by wt.	Na (by	Na (from	first break	Futectic cr. Temp.	ystallization Time	curv Temp.	e Time
(weighed)	analysis)	analysis)	° C.	° C.	sec.	°C.	sec.
11.6	10.45	51.3	365^a	·			
12.7	11.58	54.1	358	330	40		
15.00	13.95	59.4		324	960	178	50
16.35	15.06	61.5	366	328	660	182	120
18.75	16.60	64.2	377	325	390	182	180
18.35	16.76	64.5	382	326	360	182	230
18.75	17.68	65.9	388	326	240	182	260
19.60	18.35	66.9	396	326	150	181	280
18.75	18.53	67.0	397	327	120	183	280
22.10	19.78	69.0	395	330	30	179	170
21.85	20.25	69.6	396	323	20	182	180
22.10	21.08	70.6	400^{b}	• • • •		180	100
22.45	21.47	71.4	398°				
22.70	22.45	72.3	396^{d}				
24.20	22.94	72.9	395^e				
25.20	23.32	73.2	391	371	120		• • •
26.10	25.50	75.7		372	660		

Temperature at which the separation of solid solution stops: $^a350^\circ; ^b380^\circ; ^c387^\circ; ^d375^\circ; ^c370^\circ.$

position between 50 and 75 atomic per cent. of sodium. On this diagram Mathewson's data are indicated by crosses and the authors' by circles.

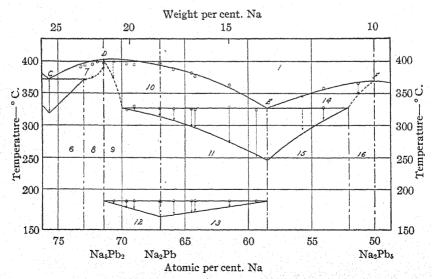
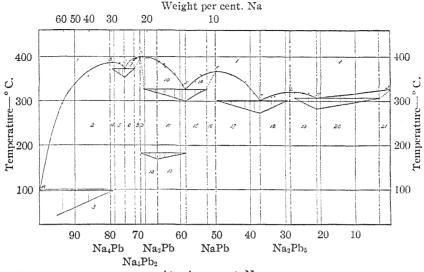


Fig. 1



Atomic per cent. Na

Fig. 2

1.	Melt	12.	$Na_{2}Pb + Na_{4}Pb$
2.	Melt + Na₄Pb	13.	Na₂Pb + NaPb
3.	$Na_4Pb + A$	14.	Melt + solid solution
4.	Solid solution (Na ₄ Pb - Na ₅ Pb ₂)	15.	NaPb + E
5.	$Na_4Pb + Na_5Pb_2 + C$	16.	Solid solution (NaPb -
6.	$Na_5Pb_2 + Na_4Pb + C$	17.	NaPb + G
7.	Melt + solid solution	18.	Na_2Pb_5+G

TARTE II

Solid solution (NaPb - Na₅Pb₂) NaPb + G

TARLE III

8. Solid solution (Na₅Pb₂ - NaPb) 9. Solid solution (NaPb - Na₅Pb₂)

19. Na₂Pb₅ + H 20. [Pb, Na₂Pb₅] + H

10. Melt + solid solution

21. Solid solution (Pb, Na₂Pb₅)

11. Na₅Pb₂ + E

The interpretation of the above data is given in the following tables.

	TUDING IL					
Pu	RE COMPOUN	os	Eur	ECTICS		
Formula	Atomic % of Na	М. р.	Compounds in entectics	tomic %	Temperature of eutectic crystallization	
NaPb	50.0	366	NaPb + Na ₅ Pb ₂	58.8	327	
Na ₅ Pb ₂	71.4	400	$Na_5Pb_2 + Na_4Pb$	76.6	372	
Na ₂ Pb	66.6	Dec. 182				

TABLE IV SOLID SOLUTIONS

Compounds in solution	NaPb + NasPb2	NaPb + Na ₄ Pb ₂	Na ₅ Pb ₂ + Na ₄ Pb
Atomic % of Na	50.0-52.0	70.0-71.4	71.4-72.4

Discussion

These results indicate that the following corrections should be made to the diagram as reported by Mathewson.

- 1. The pure compound separating from alloys of composition between 58.8 and 76.6 atomic per cent. of sodium is Na₅Pb₂ and not Na₂Pb.
- 2. This compound forms solid solutions with both NaPb and Na₄Pb and not only with the latter.
- 3. Alloys of composition between 58.8 and 71.4 atomic per cent. of sodium rearrange at 182° on cooling; the compound Na₅Pb₂ disappears, and a new compound, Na₂Pb, is formed.

It is concluded therefrom that the freezing-point diagram of lead-sodium alloys, as given in the literature should be replaced by the Fig. 2 given above.

The failure of earlier work to show the exact reaction taking place in alloys can be attributed to two reasons: (1) the insufficient number of points investigated; (2) the too rapid rate of cooling which does not enable the slight changes such as that corresponding to the formation of Na₂Pb to be detected.

Summary

It is shown that the pure compound separating from alloys of lead and sodium, whose composition is between 58.8 and 76.6 atomic per cent. of sodium, is Na₅Pb₂, this compound forming solid solutions with both NaPb and Na₄Pb.

Alloys containing 58.8 to 71.4 atomic per cent. sodium rearrange at 182° on cooling, the compound Na₅Pb₂ disappears and a new compound Na₂Pb is formed.

The complete diagram of lead sodium alloys is given corrected for the above results.

CAMBRIDGE 39. MASSACHUSETTS

NOTE

A Source of Trouble in Electrometric Measurements of Hydrogen-Ion Concentration.—If a mercury-calomel-saturated potassium chloride half cell is used for electrometric measurements of hydrogen-ion concentration, it is advisable to introduce an intermediate vessel of potassium chloride solution, which may be renewed from time to time, between the end of the tube leading from the calomel electrode and the "salt bridge" or connecting tube leading to the measuring vessel.

A reason commonly given in the literature for this precaution is that it avoids danger of the potassium chloride in the mercury electrode chamber becoming contaminated by substances that might diffuse back from the measuring vessel.

In the opinion of the authors, the real danger is this: mercuric chloride is formed in the mercury calomel cell according to the well-known reaction, $Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$. The gray color of calomel which has been in

contact with potassium chloride solutions is due to the metallic mercury which is liberated in small quantities by this reaction. Equilibrium is reached when the concentration of mercuric chloride attains a certain value; this equilibrium concentration depends partly on the concentration of potassium chloride in the electrode. The stronger the potassium chloride, the more mercuric chloride will be formed. This mercuric chloride diffuses out of the electrode through the connecting tubes and, unless an intermediate vessel is used, eventually finds its way into the hydrogen electrode chamber. Here it "poisons" the hydrogen electrode, slightly at first but more as time goes on, until no reliable measurements can be made even with freshly platinized electrodes.

A convenient test for mercuric chloride is to add a drop or two of sodium sulfide solution to the potassium chloride solution to be tested. Mercury

in sufficient concentration to poison a hydrogen electrode will give a brown coloration.

A calomel half cell has been devised for use with potentiometers having a quadrant electrometer for a null instrument, which obviates the necessity of changing the intermediate solution. In this cell the potassium chloride solution is separated from the intermediate chamber by a thin (0.05 mm.) glass bulb which conducts electricity sufficiently to charge a quadrant electrometer. See Fig. 1. This half cell cannot be

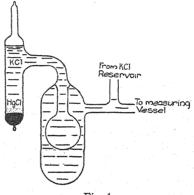


Fig. 1

used with a galvanometer as the resistance of the bulb is too high, but in case an electrometer must be used for other determinations the above electrode might be convenient for work involving measurement of hydrogen-ion concentration.

It takes several days for the glass surface potentials of the bulb to become constant after the electrode is filled and, as the potential finally reached may be slightly different from that of an ordinary calomel electrode, a correction must be made for the discrepancy. This discrepancy can easily be measured by determining the potential of the mercury electrode against the hydrogen electrode in a solution of known hydrogenion concentration.

An electrode of this type has been used in this Laboratory for several months and has given satisfactory results.

BIOPHYSICS LABORATORY HARVARD UNIVERSITY BOSTON 17, MASSACHUSETTS Received May 24, 1923 W. T. Bovie Walter S. Hughes

SYNTHESIS OF PHENYLANTHRANILIC ACIDS

By NEAL TUTTLE Received May 23, 1921

The discovery was made by Ullmann, that the mobility of halogens in the benzene ring was greatly increased by the addition of copper as catalyst. The first reaction studied in detail was the formation of phenylanthranilic acid by the action of aniline on o-chlorobenzoic acid, as represented by the following equation: C_6H_5 . $NH_2 + Cl. C_6H_4$. $COOH = C_6H_5$. $NH. C_6H_4$. COOH + HCl. Besides the copper, Ullmann added 2 equivalents of potassium carbonate, one to form the potassium salt of o-chlorobenzoic acid and the other to neutralize the hydrochloric acid resulting from the reaction. In this manner he obtained crude phenylanthranilic acid of exceptionally good quality in a yield of 97%.

In the years immediately following the discovery, this method was employed by Ullmann and his pupils in the synthesis of many substituted anthranilic acids, salicylic acids and naphthalene derivatives;² but since it attained commercial importance almost at once, it was soon buried in patents and has not often been applied in pure synthetic organic chemistry.

The present investigation deals with the action of the dialkyl-p- and m-phenylenediamines and piperidine on o-chlorobenzoic acid and its monoand dinitro derivatives which are accessible by direct nitration. The ultimate object is the conversion of these substituted phenylanthranilic acids into unsymmetrical acridones and acridines, and the following is a brief summary of the results which have been obtained.

Action of Dialkylphenylene-Diamines

On o-Chlorobenzoic Acid.—Dimethyl-p-phenylenediamine reacts with o-chlorobenzoic acid in the presence of copper to give 4'-dimethylamino-diphenylamine-2-carboxylic acid (I).

$$\begin{array}{c|c} COOH \\ \hline \\ NH \\ \hline \\ II \\ \hline \\ N(CH_3)_2 \\ \hline \\ NH \\ \hline \\ N(CH_3)_2 \\ \hline \\ NH \\ \hline \\ NH \\ \hline \\ NIII \\ \hline \end{array}$$

By heating this acid a few degrees above its melting point, it is converted almost quantitatively into 4-dimethylamino-diphenylamine (II). The properties of this compound were found to agree with those previously reported.³

When treated with coned. sulfuric acid, 4'-dimethylamino-diphenyl-

- 1 Ullmann, Ber., 38, 2211 (1905).
- ² Ullmann, Ann., (a) 355, 312 (1907); (b) 366, 79 (1909); etc.
- ² Fischer, Ber., 21, 2612 (1888).

amine-2-carboxylic acid is converted completely into 2-dimethylamino-acridone (III).

Similar results were obtained by the reaction of o-chlorobenzoic acid with diethyl-p-phenylenediamine as well as with both dimethyl- and diethyl-m-phenylenediamine.

On 5-Nitro-2-chlorobenzoic Acid.—Dimethyl-p-phenylenediamine reacts smoothly with 5-nitro-2-chlorobenzoic acid in the presence of copper to give 4-nitro-4'-dimethylamino-diphenylamine-2-carboxylic acid (IV).

It was expected that this reaction would be complete in a shorter time than the reaction between the same base and o-chlorobenzoic acid, since it is a well-established fact that a negative substituent in the ortho position with respect to the halogen in the benzene ring greatly increases its mobility, and that a negative group in para position to the halogen has a similar, though considerably smaller, labilizing effect.⁴

However, on investigating the action of dimethyl-p-phenylenediamine on 5-nitro-2-chlorobenzoic acid, the author found that the reaction required $2^1/2$ hours for completion, or approximately the same time as was required by o-chlorobenzoic acid. In the action of dimethyl-m-phenylenediamine on these two acids, as will be shown later, 5-nitro-2-chlorobenzoic acid had to be digested more than twice as long as o-chlorobenzoic acid to complete the reaction. On account of these unexpected results, the relative reactivities of the chlorine in the two cases was tested by the digestion of the acids with sodium hydroxide solution, precipitation with nitric acid and testing the filtrates with silver nitrate. o-Chlorobenzoic acid was recovered unchanged, the filtrate giving only the slightest cloudiness with silver nitrate. The filtrate obtained by the same procedure with 5-nitro-2-chlorobenzoic acid gave, however, a voluminous precipitate with silver nitrate, and the recovered acid was identified as a mixture of 5-nitro-2-chlorobenzoic acid and 5-nitrosalicylic acid.

These results prove that the nitro group in the para position does make the chlorine more labile, and the discrepancies with the dimethyl-phenyl-enediamines are probably more apparent than real. The condensation products of o-chlorobenzoic acid with the dialkyl phenylenediamines decompose to some extent during the reaction, while those of 5-nitro-2-chlorobenzoic acid appear to be more stable at the temperature of the reaction, possibly because they melt at a higher temperature.

An unexpected result was obtained when diethyl-m-phenylenediamine

4 Schöpff, Ber., 22, 3281 (1889).

acted on 5-nitro-2-chlorobenzoic acid in the presence of copper. The crude product was contaminated with a large amount of tar, as if the diamine had not entered into the reaction. After the tar had been removed by prolonged boiling of the sodium carbonate solution with animal charcoal, acidification yielded a white substance that melted sharply at 257°, without decomposition. On investigation it was found that this product had resulted from the elimination of 2 chlorine atoms from 2 molecules of 5-nitro-2-chlorobenzoic acid and was, in fact, 4,4'-dinitro-diphenyl-2,2'-dicarboxylic acid (V).

On 3,5-Dinitro-2-chlorobenzoic Acid.—As was to be expected, this acid acts so readily that the addition of copper is unnecessary.

Action of Piperidine

On o-Chlorobenzoic Acid.—When an amyl alcohol solution of piperidine and o-chlorobenzoic acid was digested in the presence of copper, a curious reaction occurred. The product was a white acid that crystallized from dil. alcohol in fine needles, melted at 155–156°, was free from chlorine and nitrogen, and proved to be salicylic acid.

Since the question immediately arose as to whether the salicylic acid owed its formation to the basic properties only of the piperidine, the process was repeated under the same conditions except that potassium hydroxide was substituted for the piperidine. In this case, however, most of the o-chlorobenzoic acid was returned unchanged, there being only qualitative indications that salicylic acid had been formed.

On 5-Nitro-2-chlorobenzoic Acid.—In amyl alcohol in the presence of copper, piperidine reacts with 5-nitro-2-chlorobenzoic acid, yielding 2-piperidino-5-nitrobenzoic acid (VI).

On 3,5-Dinitro-2-chlorobenzoic Acid.—Before either of the two reactions just described had been studied, an aqueous solution of piperidine, 3,5-dinitro-2-chlorobenzoic acid and sodium acetate was digested in the presence of copper, in the expectation that the piperidine nucleus would not enter in place of the chlorine between the nitro and carboxyl groups. The mixture became orange-colored as soon as warmed, and after the liquid had digested for 2 hours it was filled with fine green needles. These were collected and it was then observed that all the copper had disappeared. Renewed digestion of the mother liquor in the presence of fresh copper yielded more of the same needles. At the end a small amount of the copper remained undissolved. An attempted determination of the melt-

ing point of the green needles resulted in disaster, for at 320° the substance exploded violently, shattering the melting-point tube to dust. The analysis, which was made with great difficulty on account of the explosive nature of the compound, ultimately proved that the substance was the copper salt of 3,5-dinitrosalicylic acid (VII).

Labilizing Influence of the Nitro Group on Chlorine in the Benzene Ring

During the course of the syntheses already described, the author has investigated the mobility of the chlorine in o-chlorobenzoic acid and the influence of a nitro group in each of the four possible positions, 3, 4, 5 and 6. Of these 4 acids, the chlorine of 3-nitro-2-chlorobenzoic acid is the most labile, as would be expected, since the nitro and carboxyl groups occupy the two most influential positions. In the presence of copper, aniline reacts with 3-nitro-2-chlorobenzoic acid in alcoholic solution, yielding 2-nitrodiphenylamine-6-carboxylic acid (VIII).

The second acid, in order of the lability of the chlorine, should be 5-nitro-2-chlorobenzoic acid, containing 1 negative group in the *ortho* position with respect to the chlorine and the other in the *para* position. This actually seems to be the case, for the chlorine, as previously described, is removed from 5-nitro-2-chlorobenzoic acid by bases at the temperature of boiling water.

In 4-nitro- and 6-nitro-2-chlorobenzoic acid the nitro group in meta position with respect to the chlorine would be expected to exert no influence on its mobility. Since Ullmann condensed 4-nitro-2-chlorobenzoic acid with a large number of bases without commenting on the mobility of the chlorine it would appear that the nitro group of this acid is without influence on the chlorine. On the other hand, when the author digested 6-nitro-2-chlorobenzoic acid with excess of aniline in the presence of copper, it was wholly charred, and under other conditions was either charred or returned unchanged. These results seem to indicate that the nitro group in the 6 position makes the chlorine less labile than in o-chlorobenzoic acid. The difficulty of obtaining this 6-nitro acid, however, has prevented the author from completing the investigation.

The experimental part falls under the following headings: (I) dimethyl-p-phenylenediamine; (II) dimethyl-m-phenylenediamine; (III) diethyl-p-phenylenediamine; (IV) diethyl-m-phenylenediamine; (V) piperidine; (VI) investigation of the mobility of the chlorine in o-chlorobenzoic acid and its nitro derivatives.

Experimental Part

The o-chlorobenzoic acid was prepared at first by diazotization of o-toluidine and oxidation of the resulting o-chlorotoluene with potassium permanganate; but since the oxidation of o-chlorotoluene can be conveniently performed only with small quantities, this method was soon discarded in favor of the well-known process for the preparation of anthranilic acid from phthalimide.⁵ The anthranilic acid was always diazotized without being isolated.

The 5-nitro- and 3,5-dinitro-2-chloro-benzoic acids were prepared by direct nitration of o-chloro-benzoic acid.⁶

The dimethyl- and diethyl-phenylenediamines were prepared from the dialkyl anilines and were purified by distillation in a current of hydrogen. They were preserved in sealed tubes from the oxidizing action of the air.

Dimethyl-p-phenylenediamine

4'-Dimethylamino-diphenylamine-2-carboxylic Acid (I).—Three g. of o-chlorobenzoic acid, 2 g. of dimethyl-p-phenylenediamine, 3 g. of potassium carbonate, 35 cc. of amyl alcohol and about 0.2 g. of copper powder were digested over a free flame for $2^1/4$ hours. After distillation of the amyl alcohol in a current of steam, the dark green solution was boiled for about an hour with animal charcoal. It was then filtered free from charcoal and copper powder and neutralized while still hot, whereupon all the product separated at once as an amorphous, green solid, that was dried (3.1 g.) and crystallized twice from alcohol, from which it separated in pale green prisms or needles.

In the first attempts to prepare this acid, copper was employed which had been made by the addition of zinc to a solution of copper sulfate, and no pure product could be isolated. Substitution of the so-called "molecular copper," which can be bought in the market, yielded a good product at once.

Since dimethyl-p-phenylenediamine becomes impure so rapidly in contact with the air, a steady stream of dry hydrogen was passed through the apparatus during the digestion.

Analyses. Subs., 0.1350: 12.5 cc. of N_2 (14°, 753 mm.). Subs., 0.1208: CO_2 , 0.3109; H_2O , 0.0688. Calc. for $C_{15}H_{16}O_2N_2$: C, 70.5; H, 6.3, N, 10.9. Found: C, 70.2; H, 6.3; N, 10.8.

The substance melts at 216° with decomposition. It is practically insoluble in water and only slightly soluble in xylene and alcohol. It dissolves more readily in acetic acid but does not separate on cooling.

4-Dimethylamino-diphenylamine (II).—One g. of 4'-dimethylamino-diphenylamine-2-carboxylic acid was heated in an oil-bath at about 220° until the evolution of carbon dioxide ceased. When cold the dark residue was extracted with hot alcohol, and the purple solution decolorized by boiling with animal charcoal. Concentration and cooling yielded fine, white needles, and two more crystallizations raised the melting point to 130°, that found by O. Fischer.³

2-Dimethylamino-acridone (III).—Two g. of 4'-dimethylamino-diphenylamine-2-carboxylic acid was dissolved in 20 g. of concd. sulfuric acid and the solution heated to 100°. It became fluorescent at once, and after 10 minutes was poured into 500 cc. of

⁵ Compt. rend., 10, 6 (1901); etc.

⁶ Graebe, Ann., 276, 40 (1893). Holleman and de Bruyn, Compt. rend., 20, 209 (1911). Ref. 2b.

water. Neutralization with ammonia yielded the acridone as a yellow, amorphous precipitate; yield, about 95%. It crystallized from alcohol in small, bright yellow clusters; m. p., $289-290^{\circ}$.

Analyses. Subs., 0.1024: CO₂, 0.2842; H₂O, 0.0550. Subs., 0.1054: 10.6 cc. of N₂ (16°, 760 mm.). Calc. for $C_{15}H_{14}ON_2$: C, 75.63; H, 5.88; N, 11.76. Found: C, 75.68; H, 5.96; N, 11.72.

This acridone is only slightly soluble in all organic solvents. In alcohol and concd. sulfuric acid the fluorescence is blue; in acetic acid, green.

4-Nitro-4'-dimethylamino-diphenylamine-2-carboxylic Acid (IV).—Three g. of 5-nitro-2-chlorobenzoic acid, 2 g. of dimethyl-p-phenylenediamine, 2 g. of potassium carbonate, 35 cc. of amyl alcohol and about 0.2 g. of copper were digested for $2^1/_2$ hours. The amyl alcohol was then distilled with steam, and the red solution, after purification with charcoal, was neutralized with hydrochloric acid. The brown amorphous product was crystallized twice from alcohol, forming small, coppery needles; m. p., 234–235°.

Analyses. Subs., 0.1058: CO₂, 0.2330; H₂O, 0.0486. Subs., 0.1000: 11.8 ec. of N₂ (15°, 758 mm.). Calc. for $C_{16}H_{15}O_4N_3$: C, 59.8; H, 4.98; N, 13.95 Found: C, 60.05; H, 5.10; N, 13.8.

When the process just described was carried out in an atmosphere of hydrogen, the yield of crude product amounted to only 50%. Without the hydrogen, however, the yield was 75%.

This synthesis was also accomplished by digesting for 6 hours a solution of 2 g. of 5-nitro-2-chlorobenzoic acid, 1.35 g. of dimethyl-p-phenylenediamine and 2.7 g. crystallized sodium acetate in 20 cc. of water, with about 0.2 g. of copper. The product, however, was much more tarry and difficult to purify.

2,4-Dinitro-4'-dimethylamino-diphenylamine-6-carboxylic Acid.—One and sixtenths g. of dimethyl-p-phenylenediamine was added, drop by drop, to a solution of 3 g. of 3,5-dinitro-2-chlorobenzoic acid and 3.3 g. of crystallized sodium acetate in 20 cc. of water. A vigorous reaction took place, the mixture became brown, and a yellow precipitate separated; yield, 100%. The product was collected and purified by crystallization of the hydrochloride from dil. hydrochloric acid. The hydrochloride forms reddish-brown plates, is sparingly soluble in water and dil. hydrochloric acid, and melts gradually at 240–260°.

Analysis. Subs., 0.0806: 10.1 cc. of N_2 (13°, 754 mm.). Calc. for $C_{15}H_{15}O_6N_4C1$: N, 14.64. Found: 14.81.

A part of the pure hydrochloride was dissolved in water and the free 2,4-dinitro-4'-dimethylamino-diphenylamine-6-carboxylic acid precipitated with sodium acetate. Obtained in this manner, the acid was a bright yellow, amorphous powder, melting at 253° with decomposition.

Analysis. Subs., 0.1132: 15.5 cc. of N_2 (16°, 760 mm.). Calc. for $C_{15}H_{14}O_5N_4$: N, 16.18. Found: 15.96.

Dimethyl-meta-phenylenediamine

3'-Dimethylamino-diphenylamine-2-carboxylic Acid.—Three g. of o-chlorobenzoic acid, 2 g. of dimethyl-m-phenylenediamine, 3 g. of sodium carbonate, 35 cc. of amyl alcohol and 0.2 g. of copper were digested in an atmosphere of hydrogen for 2:05 hours. After removal of the amyl alcohol with steam and treatment of the solution with animal charcoal, the clear brown solution was cooled in ice and neutralized. The pale brown precipitate was collected rapidly and dissolved in hot 50% alcohol. As this cooled, pale brown needles separated, which after two more crystallizations were colorless and melted at 155°, without decomposition.

Analyses. Subs., 0.1120: CO₂, 0.2880; H_2O , 0.0644. Subs., 0.1096: 10.5 ec. of N_2 (18°, and 755 mm.). Calc. for $C_{15}H_{16}O_2N_2$: C, 70.31; H, 6.25; N, 10.93. Found: C, 70.12; H, 6.38; N, 10.99.

4-Nitro-3'-dimethylamino-diphenylamine-2-carboxylic Acid.—This acid was obtained by digestion for 5 hours of a mixture of 3 g. of 5-nitro-2-chlorobenzoic acid, 2 g. of dimethyl-m-phenylenediamine, 2 g. of sodium carbonate, 35 cc. of amyl alcohol and about 0.2 g. of copper. After recovery of the amyl alcohol by distillation with steam and purification of the solution by boiling with animal charcoal, the product was precipitated by neutralizing the solution with hydrochloric acid. It was crystallized thrice from alcohol, forming small, greenish-brown needles without definite melting point. Heated gradually to 300°, it sintered and became black without actually melting, but when dipped into a bath at 247° it melted sharply, with decomposition.

Analyses. Subs., 0.1062: CO₂, 0.2336; H₂O, 0.0485. Subs., 0.1248: 15.3 ec. of N₂ (21°, 756 mm.). Calc. for $C_{15}H_{15}O_4N_3$: C, 59.80; H, 4.98; N, 13.95. Found: C, 59.98; H, 5.07; N, 13.88.

2,4-Dinitro-3'-dimethylamino-diphenylamine-6-carboxylic Acid.—This acid was prepared in two different ways. (1) A solution of 3.7 g. of 3,5-dinitro-2-chlorobenzoic acid and 2 g. of dimethyl-m-phenylenediamine in 80 cc. of absolute alcohol, was digested under a reflux condenser for 35 minutes. As the mixture cooled, fine green needles separated (3.5 g.), and cautious addition of water to the mother liquor yielded more needles (0.4 g.). Obtained thus, the acid is quite pure, as shown by analysis.

Analysis. Subs., 0.1445: 20.1 cc. of N_2 (19°, 766 mm.). Calc. for $C_{15}H_{14}O_6N_4$: N, 16.18. Found: 16.12.

The substance turned dark when heated above 300° but did not melt. It is very sparingly soluble in all organic solvents except alcohol. (2) A solution of 3 g. of 3,5-dinitro-2-chlorobenzoic acid, 1.6 g. of dimethyl-m-phenylenediamine, and 3.3 g. of crystallized sodium acetate in 20 cc. of water was digested under a reflux condenser for 1 hour. The product began to separate very soon and at the end entirely filled the volume of the liquid; yield, 100%. Made in this way, the acid is amorphous. In the present case it was dissolved in hot, dil. hydrochloric acid and as this solution cooled the hydrochloride separated in green needles.

Analysis. Subs., 0.1518: 19.2 cc. of N $_2$ (22°, 753 mm.). Calc. for $C_{15}H_{18}O_6N_4C1$: N, 14.64. Found: 14.18.

When heated to 320° the hydrochloride sintered but did not melt.

Diethyl-para-phenylenediamine

4'-Diethylamino-diphenylamine-2-carboxylic Acid.—Two g. of o-chlorobenzoic acid, 2 g. of diethyl-p-phenylenediamine, 2 g. of sodium carbonate, 35 cc. of amyl alcohol and about 0.2 g. of copper were digested for 90 minutes. After distillation with steam and treatment with animal charcoal the clear brown solution was cooled to 0° and neutralized slowly. A light blue substance separated which did not become tarry on standing for 2 hours in the solution at 0°. As soon as it was collected, however, it became gummy and black. All attempts to crystallize the free acid, its sodium salt and its acid salts were unsuccessful.

4'-Diethylamino-4-nitro-diphenylamine-2-carboxylic Acid.—A mixture of 2.5 g. of 5-nitro-2-chlorobenzoic acid, 2 g. of diethyl-p-phenylenediamine, 2.5 g. of sodium carbonate, 35 cc. of amyl alcohol and about 0.2 g. of copper was digested for $2^1/2$ hours. The amyl alcohol was recovered by distillation with steam and the solution of the sodium salt freed from a small amount of tar by boiling it with animal charcoal. Neutralization then yielded an olive-green precipitate that weighed 3.1 g.; yield, 78%. This

was crystallized twice from alcohol, separating the second time in fine brown needles; m. p., $239-240^{\circ}$.

Analyses. Subs., 0.1112: CO₂, 0.2518; H_2O , 0.0601. Subs., 0.1125: 12.3 cc. of N_2 (17°, 750 mm.). Calc. for $C_{17}H_{19}O_4N_3$: C, 62.00; H, 5.77; N, 12.76. Found: C, 61.59; H, 5.98; N, 12.51.

4'-Diethylamino-2,4-dinitrodiphenylamine-6-carboxylic Acid.—A solution of 3 g. of 3,5-dinitro-2-chlorobenzoic acid, 2 g. of diethyl-p-phenylenediamine and 3.5 g. of crystallized sodium acetate in 20 cc. of water was warmed, whereupon a precipitate appeared, and after the liquid had been boiled for 5 minutes it was entirely filled with a brown amorphous solid. When this was cold, 4 g. of product was collected and dissolved in hot, dil. hydrochloric acid; the solution as it cooled deposited the hydrochloride in orange-colored flakes; m. p., 252–253°.

Analysis. Subs., 0.0950: 10.9 cc. of N_2 (13°, 754 mm.). Calc. for $C_{17}H_{19}O_6N_4Cl$: N, 13.64. Found: 13.44.

A portion of the pure hydrochloride was dissolved in hot water and the free acid precipitated with sodium acetate.

Analysis. Subs., 0.1135: 14.7 cc. of N_2 (16°, 760 mm.). Calc. for $C_{17}H_{18}O_6N_4$: N, 14.97. Found: 15.10.

The substance was a bright yellow powder; m. p., 259°. It is either insoluble or very sparingly soluble in ethyl alcohol, methyl alcohol, benzene, acetone, acetic acid, chloroform, xylene, toluene, ether, carbon tetrachloride or water. It dissolved in boiling pyridine but did not separate when the solution was cooled.

Diethyl-meta-phenylenediamine

 $3^\prime\text{-Diethylamino-diphenylamine-2-carboxylic}$ Acid.—A mixture of 5 g. of o-chlorobenzoic acid, 5 g. of diethyl-m-phenylenediamine, 5 g. of sodium carbonate, 60 cc. of amyl alcohol and about 0.2 g. copper was digested for 1 hour. The amyl alcohol was recovered by distillation with steam and the solution was boiled with animal charcoal. After this had cooled to 0° , neutralization yielded a dark blue precipitate, which did not collect into a tar as long as it remained in suspension. When collected on the filter, however, it became black and gummy at once. As in the case of its isomer previously described, neither the acid nor any of its salts could be obtained in a pure state.

Action of Diethyl-m-phenylenediamine on 5-Nitro-2-chlorobenzoic Acid. 4,4'-Dinitrodiphenyl-2,2'-dicarboxylic Acid (V).—A mixture of 4 g. of diethyl-m-phenylenediamine, 5 g. of 5-nitro-2-chlorobenzoic acid, 5 g. of sodium carbonate, 60 cc. of amyl alcohol and about 0.2 g. of copper was digested for 31/2 hours. After removal of the amyl alcohol with steam, the liquid contained a large amount of tarry matter which was completely removed by long boiling with animal charcoal. Acidification of the pale yellow solution thus obtained yielded an almost pure product. This was collected and crystallized twice from alcohol, from which it separated in thick, white needles. Dried at 100° the glossy needles lost water of crystallization and then melted at 257°.

Analyses. Subs., 0.1062: CO₂, 0.1961; H₂O, 0.0249. Calc. for $C_{14}H_8O_8N_2$: C, 50.6; H, 2.4. Found: C, 50.4; H, 2.6.

The substance is fairly soluble in hot water and crystallizes with 1 molecule of water of crystallization, which it loses completely only at 150-160°, as stated by Schultz,

Analyses. Subs., 0.3457, 0.6397: loss at 160°, 0.0195, 0.0355. Calc. for $C_{14}H_8O_8-N_2.H_2O$: H_2O , 5.14. Found: 5.64, 5.55.

As final confirmation of the identity of this acid, the dimethyl ester was prepared by the addition of 5 cc. of dimethyl sulfate to a solution of 1 g. of anhydrous 4,4'-dinitro-

⁷ Schultz, Ann., 196, 26 (1879).

diphenyl-2,2'-dicarboxylic acid in 30 cc. of 2 N sodium hydroxide solution, vigorous agitation of the mixture for 4 hours and after 1 hour collection of the white solid which had separated; m. p., 166–172°. After two crystallizations of the substance from methyl alcohol the melting point was 177–178°, which is that reported by Schultz.

3'-Diethylamino-2,4-dinitro-diphenylamine-6-carboxylic Acid.—A solution of 3 g. of 3,5-dinitro-2-chlorobenzoic acid and 2 g. of diethyl-m-phenylenediamine in 90 cc. of 99% alcohol, colorless at first, became red as soon as it was warmed, and after 2 minutes' boiling yellow needles separated. After 5 minutes the solution was cooled and 2 g. of bright yellow needles was collected, washed with alcohol and dried; m. p., 220° (decomp.).

Analysis. Subs., 0.1372: 17.5 cc. of N_2 (14°, 758 mm.). Calc. for $C_{17}H_{18}O_6N_4$: N, 14.97. Found: 14.96.

Piperidine

Action of Piperidine on o-Chlorobenzoic Acid in the Presence of Copper. Formation of Salicylic Acid.—A mixture of 5.6 g. of o-chlorobenzoic acid, 3 g. of piperidine, 6 g. of sodium carbonate, 35 cc. of amyl alcohol and about 0.2 g. of copper was digested with vigorous stirring for 6 hours. After recovery of the amyl alcohol by distillation with steam, the bright green solution, containing only the copper powder undissolved, was treated with animal charcoal, filtered and the filtrate evaporated to about 50 cc. When this concentrated solution was acidified with hydrochloric acid, a slightly yellow precipitate separated. To remove the color the product was dissolved in dil. sodium carbonate solution and again treated with animal charcoal. Acidification then yielded a pure white acid, which crystallized from 25% alcohol in fine, white needles; m. p., 155–156°.

Analyses. Subs., 0.1131: CO_2 , 0.2566; H_2O , 0.0462. Calc. for $C_7H_6O_3$: C, 60.86; H, 4.34. Found: C, 61.87; H, 4.55.

A mixed melting point with pure, known salicylic acid of melting point 156.5° gave 156.5° unchanged.

2-Piperidino-5-nitrobenzoic Acid (VI).—A mixture of 2.4 g. of 5-nitro-2-chlorobenzoic acid, 1 g. of piperidine, 2 g. of sodium carbonate, 20 cc. of amyl alcohol and about 0.2 g. of copper was digested and vigorously stirred for half an hour. After the first 15 minutes the solution was orange-colored and filled with a white solid, and digestion for an additional 15 minutes made no apparent change. The amyl alcohol was then recovered by distillation with steam and the filtered solution acidified. The yellow precipitate thus formed was collected and crystallized thrice from alcohol, the hot solution being treated each time with animal charcoal. The 2-piperidino-5-nitrobenzoic acid was thus obtained as very pale yellow, well-formed rhombic crystals; m. p., 200–202°.

Analyses. Subs., 0.0908: CO_2 , 0.1929; H_2O , 0.0467. Subs., 0.1221: 12 cc. of N_2 (15°, 758 mm.). Calc. for $C_{12}H_{14}O_4N_2$: C, 57.6; H, 5.6; N, 11.2. Found: C, 57.93; H, 5.71; N, 11.47.

Action of Piperidine on 3,5-Dinitro-2-chlorobenzoic Acid. Formation of 3,5-Dinitrosalicylic Acid.—A mixture of 3 g. of 3,5-dinitro-2-chlorobenzoic acid, 1 g. of piperidine, 3.3 g. of crystallized sodium acetate, 50 cc. of water and about 0.2 g. of copper was digested for 3 hours. The solution became orange colored at once, but gradually turned pale yellow, and green needles soon began to separate. After 2 hours, the process was interrupted to collect these needles (2 g.). Since the copper had entirely disappeared, more was added and the digestion continued for another hour. The total yield was 3 g. of the copper salt of 3,5-dinitrosalicylic acid.

The product was crystallized from very dilute alcohol and dried at 100°. As described in the introduction, this copper salt explodes violently at about 320°.

Analysis. Subs., 0.1309: 11 cc. of N_2 (17°, 747 mm.). Calc. for $C_{14}H_6O_{14}N_4Cu$: N, 10.8. Found: 9.6.

Since the analysis for nitrogen was of questionable accuracy on account of the explosive nature of the compound, an analysis for copper was undertaken. Difficulties arose at once, however. After a solution of the copper salt in coned. mineral acids had been boiled for some time, qualitative tests of the solution did not indicate the presence of copper. Furthermore, boiling with dil. sodium hydroxide deposited no copper oxide, and dry ignition was obviously out of the question. The procedure finally adopted was as follows.

In a porcelain crucible 0.4466 g. of substance was moistened with a few drops of coned. sulfuric acid and very cautiously ignited until all the organic matter had been decomposed. The black residue was then readily dissolved in about 5 cc. of coned. nitric acid and the solution transferred to a beaker. The nitric acid was expelled by several evaporations with excess of hydrochloric acid, the solution diluted with water and the copper precipitated with sodium hydroxide.

Analysis. Subs., 0.5001: CuO, 0.0682. Cale. for $C_{14}H_6O_{14}Cu$: Cu, 12.3. Found: 10.9.

Thus the percentages found for both nitrogen and copper were considerably lower than the calculated percentages for the copper salt of 3,5-dinitrosalicylic acid. In explanation of this discrepancy, it was found that the specimen employed in both analyses still contained 10.7% of water of crystallization, which it lost completely only at 180° . When allowance is made for this 10.7% in the calculations, the analyses may be restated as follows.

Analyses. Subs., 0.1169: 11 cc. of N_2 (17°, 747 mm.). Subs., 0.4466: CuO, 0.0682. Calc. for $C_{14}H_6O_{14}N_4Cu$: N, 10.8; Cu, 12.3. Found: N, 10.68; Cu, 12.19.

A later determination of the water of crystallization gave the following result.

Analysis. Subs., 0.8482: loss at 180°, 0.0870. Calc. for $C_{14}H_6O_{14}Cu.3H_2O$: H_2O , 10.1. Found: 10.2

In order to confirm the identity of this compound as the copper salt of 3,5-dinitro-salicylic acid, 1.9890 g., dried at 200°, was boiled with 50 cc. of 20% potassium hydroxide solution for 2 hours. The solution became a deep red almost at once and copper oxide soon began to separate. While the mixture was still hot, the copper oxide was removed (0.2760 g.; Cu, 11.1%). The filtrate and first wash waters were evaporated to a small volume and cooled, whereupon red needles separated. These were twice recrystallized from a small volume of water containing about 10% of alcohol, and dried at room temperature.

Analysis. Subs., 0.3999: loss at 170°, 0.0212. Calc. for $C_7H_2O_7N_2K_2.H_2O$: H_2O , 5.6. Found: 5.3.

This is in agreement with the statement of Hübner.8

When the mother liquors of the dipotassium salt were poured into an excess of dil. hydrochloric acid, the monopotassium salt separated as a yellow powder. After the solution of the monopotassium salt had been boiled for an hour with the excess of hydrochloric acid and concentrated to a small volume, cooling the mixture in ice deposited 3,5-dinitrosalicylic acid. Repeated crystallizations from very dilute hydrochloric acid raised the melting point only to 170°, in comparison with 173° found by previous investigators.

The pure acid was dissolved in 25 cc. of absolute alcohol, the solution saturated with dry hydrogen chloride and allowed to stand overnight. When the mixture was poured into water, a brown oil separated which soon solidified. This ethyl ester crystallized from alcohol in small coppery needles and melted at 99°, as stated by Hübner.8

⁸ Hübner, Ann., 195, 47 (1879).

Finally, the solutions of the copper salt, the free acid and the ethyl ester gave a red color with ferric chloride.

Investigation of the Mobility of the Chlorine in ortho-Chlorobenzoic Acid and its Nitro Derivatives

o-Chlorobenzoic Acid.—A mixture of 2 g. of o-chlorobenzoic acid (m. p., 141°), 2 g. of potassium hydroxide and 20 cc. of water was digested for 4 hours. The solution was acidified with nitric acid, yielding then o-chlorobenzoic acid which melted at 140°. The filtrate gave no precipitate with silver nitrate. When this experiment was carried out in the presence of copper the result was the same.

In this connection may be stated the results of an attempt to convert o-chlorobenzoic acid into salicylic acid by means of potassium hydroxide instead of piperidine.

One g. of potassium hydroxide, 2 g. of o-chlorobenzoic acid, 2 g. of sodium carbonate, 20 cc. of amyl alcohol and about 0.2 g. of copper were digested together for 6 hours. After the amyl alcohol had been removed by distillation with steam and the solution filtered to free it from undissolved copper, acidification with nitric acid yielded 1.9 g. of o-chlorobenzoic acid; m. p., 137–138°. Since the filtrate gave a slight precipitate with silver nitrate it was extracted with ether. Evaporation of the ether left about 0.1 g. of white acid, which after crystallization from water melted at 131–132°. Its solution gave a red coloration with ferric chloride; it was therefore probably a mixture of o-chlorobenzoic acid and salicylic acid. The amount was considered too small to permit a separation of the 2 acids.

5-Nitro-2-chlorobenzoic Acid.—Two g. of 5-nitro-2-chlorobenzoic acid, 2 g. of potassium hydroxide and 20 cc. of water were digested together for 4 hours. Acidification with nitric acid then yielded an acid which melted over a wide range, from 155° to 210°. By several crystallizations from a rather large amount of water, 5-nitrosalicylic acid was obtained in fine, pale yellow needles; m. p., 227°.

3-Nitro-2-chlorobenzoic Acid. Formation of 2-Nitrodiphenylamine-6-carboxylic Acid.—One g. of 3-nitro-2-chlorobenzoic acid, 5 g. of aniline, 0.7 g. of potassium carbonate, 10 cc. of ethyl alcohol and about 0.2 g. of copper were digested for 1 hour. After the excess of aniline had been removed by distillation with steam the solution was filtered and acidified with hydrochloric acid. The bright red alkaline solution hereupon became yellow, and the product separated in yellow clusters. After several crystallizations from dil. alcohol the substance melted at 194°.

Analysis. Subs., 0.0735: 6.7 cc. of N_2 (11°, 758 mm.). Calc. for $C_{13}H_{10}O_4N_2$: N, 10.85. Found: 10.89.

Summary

- 1. In most instances o-chlorobenzoic acid and its nitro derivatives reacted with the dimethyl- and diethyl-p- and m-phenylenediamines to yield the expected products. The only exception was the reaction of 5-nitro-2-chlorobenzoic acid with diethyl-m-phenylenediamine which gave 4,4'-dinitrodiphenyl-2, 2'-dicarboxylic acid.
- 2. With piperidine these acids yielded chiefly unexpected products. 5-Nitro-2-chlorobenzoic acid alone reacted in the expected manner. o-Chlorobenzoic acid yielded salicylic acid and 3,5-dinitro-2-chlorobenzoic acid yielded 3,5-dinitrosalicylic acid.

MOAB, UTAH

(5)

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

THE CONDENSATION PRODUCTS OF METHYLETHYL KETONE¹

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Introduction

The action of various condensing agents upon acetone has been studied by numerous investigators.²

The most important of these condensation products of acetone are mesityl oxide, mesitylene, phorone, and isophorone. The following equations summarize the action of various reagents upon acetone.

In the light of the very interesting work that has been done on the condensation of acetone, it seemed important that corresponding investigations be made on methylethyl ketone, which is now available in large quantities.

 $4 (CH_3)_2CO - 3 H_2O = Xylitone.$ (Constitution unknown.)

A study of the literature shows that a compound assumed to be a homolog of mesityl oxide was first prepared by Pawlow² by the action of propionyl chloride upon zinc dimethyl and methylethyl ketone in the cold, and later by Schramm⁴ by the action of sodium on methylethyl ketone in benzene solution. The substance Schramm obtained was a nearly colorless liquid of peppermint-like odor, boiling at $163-165^{\circ}$ (729 mm.). The only derivative of this substance that Schramm attempted to obtain was a dark colored oil that easily decomposed, formed by the action of bromine. Schramm also obtained an impure ketone with a camphor-like odor, of the probable formula $C_{12}H_{20}O$, boiling at $248-253^{\circ}$, which he considered a trimethyl phorone. Descudé,⁵ working with zinc chloride upon a mixture of acetyl chloride and methylethyl ketone, obtained a liquid of peppermint-like odor boiling at $167-168^{\circ}$, evidently the same as that obtained by Schramm, and a second liquid boiling at $248-253^{\circ}$ which he considered to be a homolog of

¹ From a thesis submitted to the Faculty of the Graduate School of the University of Colorado by W. Warren Howe in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² (a) Kane, Pogg. Ann., 44, 475 (1838). (b) Fittig, ibid., 110, 35 (1859).
(c) Von Baeyer, ibid., 140, 301 (1866). (d) Claisen, ibid., 180, 1 (1876). (e) Bredt and Rübel, ibid., 289, 10 (1895); 299, 160 (1897). (f) Kerp and Müller, ibid., 290, 123 (1896); (g) 299, 193 (1897). (h) Knoevenagel, ibid., 297, 185 (1897). (i) Crossley and Gilling, J. Chem. Soc. Abs., 95, 19 (1909). (j) Pinner, Ber., 15, 589 (1882).

³ Pawlow, Ann., 188, 138 (1877).

⁴ Schramm, Ber., 16, 1581 (1883).

⁵ Descudé, Ann. chim., [7] 29, 494 (1903).

phorone. This second liquid was also studied by Braun and Kittel⁶ who recorded a boiling point of 256° and found that, assuming a formula of $C_{12}H_{20}O$, it added 4 bromine atoms. They therefore concluded that the compound had two double bonds and arbitrarily assigned to it the formula $CH_3.CO.C(CH_3) = C(CH_3).C(CH_3) = C(CH_3).CH_2.CH_3.$

The present research was undertaken to study first, the action of hydrogen chloride and of sulfuric acid upon methylethyl ketone, and second, the action of sodium ethylate upon methylethyl ketone.

Theoretical Part

The theoretical possibilities are much greater for the formation of condensation products from methylethyl ketone than from acetone. From methylethyl ketone we derive for the homologs of mesityl oxide 2 different structural oxides, each of which may occur in a *cis* and a *trans* form.

Each of these 4 oxides in turn by condensing with a third molecule of methylethyl ketone may yield 2 different structural homologs of phorone. The cis and trans forms of these structural isomers are reciprocally identical. It is found, therefore, that there are 4 possible different isomers of the phorone thus obtained. The following tables show the structures of these isomes.

The isomeric homologs of phorone III, IV, V and VI may in turn suffer ring formation producing isomeric homologs of isophorone. A detailed study will show that 4 structurally different isomers, all homologs of isophorone, are possible. Their structures are indicated as follows.

⁶ Braun and Kittel, Monatsh., 27, 804 (1906).

Similarly, a great number of isomeric homologs of xylitone could be worked out from a theoretical standpoint.

In this paper, for the convenience of nomenclature, we shall give the name "homomesityl oxide" to the homologs of mesityl oxide, the name "homophorone" to the homologs of phorone, and the name "homo-isophorone" to the homologs of isophorone. On oxidation homomesityl oxide I should yield propionic acid, and homomesityl oxide II should yield acetic acid, and a mixture of I and II should yield a mixture of acetic and propionic acids.

Syntheses carried out in the manner of Knoevenagel^{2h} should throw light on the constitution of homo-isophorones, while molecular-refraction data should be valuable confirmatory evidence. If a homomesityl oxide has been shown to have the structure I, it should, when condensed with methyl aceto-acetic ester by Knoevenagel's method, yield homo-isophorones with structures corresponding to the isomers γ and δ , thus:

A study of the reactions, therefore, leads to the following.

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(1)	Homomesityl oxide I		
	+ methyl aceto-acetic ester ->	homo-isophorones γ and δ .	(7)
(2)	Homomesityl oxide II		
	+ methyl aceto-acetic ester ->	homo-isophorone α only.	(8)
(3)	Homomesityl oxide I		134
1	+ propionyl acetic ester ->	homo-isophorone β only.	(9)
(4)	Homomesityl oxide II		
	+ propionyl acetic ester ->	homo-isophorones γ and δ .	(10)

It will be shown in the experimental part of this paper that only one compound corresponding to a homomesityl oxide occurs among the condensation products obtained by using sulfuric acid or sodium ethylate as condensing agent, and that the homomesityl oxide yields only propionic acid on oxidation with permanganate. It must, therefore, be homomesityl oxide I. It will also be shown that 3 other condensation products gave analytical results and molecular weights such that they must have the empirical formula $C_{12}H_{20}O$, and must, therefore, be either homophorones or

homo-isophorones. Condensation of the experimentally obtained homo-mesityl oxide with methyl aceto-acetic ester after the method of Knoevenagel gave a mixture of 2 compounds which on fractionation under diminished pressure were found to be identical with two of the condensation products having the formula $C_{12}H_{20}O$. These two compounds boiling at $256-260^{\circ}$ and $280-285^{\circ}$, respectively, at 630 mm., must therefore have the structures γ and δ , or δ and γ (according to Equation 7 given above).

The non-occurrence of homomesityl oxide II among the condensation products from either acid or alkaline condensing agents shows that this homomesityl oxide must have been used up during the reactions to form homophorones by condensing with another molecule of methylethyl ketone.

If we assume the exaltation of the molecular refraction of homo-isophorone to be the same as that for isophorone, this compound should show a molecular refraction, M, of 56.08. Similarly, homophorone should show a molecular refraction of 59.7. The actually observed molecular refraction of the third product of condensation showing an empirical formula $C_{12}H_{20}O$ and boiling point 206–210°, was 57.72. This value, while not as high as that calculated above, is altogether too high for a homo-isophorone. Also, the fact that this compound shows the next higher boiling point in the series to homomesityl oxide would point to its being a homophorone. The following table shows the boiling points of the two series (acetone and methylethyl ketone).

Mesityl oxide	127-130°	Homomesityl oxide	156-160°
Phorone	197	Compound in question	206-210
Isophorone	213-215	Homo-isophorone γ or δ	256-260
		Homo-isophorone δ or γ	280-285

Moreover, acetone with hydrochloric acid acting as a condensing agent yields only mesityl oxide and phorone. Similarly, hydrochloric acid acting on methylethyl ketone yields only homomesityl oxide and the compound in question, as will be shown by the experimental results. It is evident that further work must be done on this compound to settle definitely whether or not it is a homophorone or a homo-isophorone. What evidence we have points to its being a homophorone.

Experimental Part

The methylethyl ketone was a very pure, water-white product containing traces of acetone. On distillation, all but a small fraction of the product passed over at 70-73° (625 mm.).

Condensation of Methylethyl Ketone under the Influence of Dry Hydrogen Chloride

Into 160 g. of methylethyl ketone, packed in ice, dry hydrogen chloride was passed not too rapidly until the liquid was completely saturated. The cork of the container was tied down so as to leave the liquid under a slight pressure. The mixture was allowed to stand for 30 days. The ketone was then washed with water to remove the excess of

acid, and poured into alcoholic potassium hydroxide; water was added, and an oily layer separated that was taken up with ether. The ether solution was dried over anhydrous sodium sulfate. After the ether was distilled an oily mixture remained that was fractionated, first at atmospheric pressure (625 mm.) up to 165°, and then under diminished pressure (15 mm.). Homomesityl oxide and homophorone only were obtained. The results are contained in Table I.

Condensation of Methylethyl Ketone under the Influence of Sulfuric Acid

Experiments were carried out with furning c. P. sulfuric acid containing, 20% excess of sulfur trioxide, and with a c. P. coned. acid, d. 1.84. It was found that the action of fuming acid on methylethyl ketone for 10 to 12 days was the same as that of the coned, acid during 16 to 20 days. Since an observation of the final effect of sulfuric acid on the ketone was desired the action was allowed to proceed over a long period. siderable amount of homomesityl oxide forms with the furning acid in 2 hours or with the coned, acid in 24 hours. The fuming acid will give a fair yield of homophorones in 4 days and the concd. acid in 7 days. In any case, the acid mixture was poured into two 2liter beakers half filled with snow or chipped ice, and a concd. solution of potassium hydroxide was added gradually until the black oil separated completely. The oil was not soluble in dil. sulfuric acid; therefore the dilute acid, colored with green to golden fluorescent sulfonic acids, was discarded. The black oil was dissolved in 5 times its volume of ether; the ether solution was then washed repeatedly with dil. sodium hydroxide solution and finally with water. This treatment changed the ether solution from a black to a beautiful golden-brown. After the ether had been dried with calcium chloride it was distilled and the oil fractionated, first at atmospheric pressure (625 mm.) and then under diminished pressure (15 mm.). Typical results are shown in Table I.

Many difficulties were encountered in using acid condensation agents with methylethyl ketone. In the experiments with both the hydrochloric and the sulfuric acids, addition products were formed that contaminated every fraction. After every precaution, traces of acid (hydrochloric or sulfurous) were found to come over during a distillation, and apparently pure fractions became dark colored on standing. The action of sodium ethylate, on the other hand, gave pure products.

Condensation of Methylethyl Ketone under the Influence of Sodium Ethylate

Pure sodium ethylate was prepared by the gradual addition of the calculated amount of absolute alcohol to sodium wire covered with a large volume of ether. Enough of the condensing agent was used to furnish sodium in the proportion 1 Na: 4 C₂H₅.CO.CH₅. The ethylate crystals were added in portions to the slightly cooled ketone. The mixture was then allowed to stand at ordinary temperatures protected from moisture for 3 or 4 weeks. When the sodium ethylate was not prepared pure, reddish, water-soluble waste products were obtained. The reaction mixture was then dissolved in 4 times its volume of ether and the ether solution washed 5 or 6 times with water until the wash water was neutral. The solution was dried over calcium chloride overnight, the ether distilled and the oil fractionated, first at atmospheric pressure until the homomesityl oxide was removed, and then at diminished pressure. Typical results are shown in Table I.

The results in this table are not "averages" but are from actual experiments selected from 20 to 30 such experiments.

Fractions 1, 2 and 3 were always obtained under normal pressure (625 mm. at Boulder).

Fractions 4 to 10, inclusive, were obtained at diminished pressure (15 mm.).

On repeated fractionation, Fraction 3 yielded pure homomesityl oxide; Fraction 4 yielded pure homophorone; Fractions 6 and 8 yielded the pure homo-isophorones.

TABLE I RESULTS HC1 Fuming Sodium H₂SO₄ ethylate G. Main Temperature C. H2SO4 gas G. Fraction G. constituent 40 60 56 12 methylethyl ketone 60-90 1 2 90-140 24 10 12 24 3 140 - 16560 49 35 27 homomesityl oxide 48 62 4 90 - 1309 58 homophorone 5 130-145 16 40 50 70 75 145-160 36 homo-isophorone 6 7 160-170 13 15 12 8 170-180 37 45 34 homo-isophorone 24 38 9 180-200 45 200-230 50 50 58 10 and above 184 250 dry gas 450 Character of agent 20% ex. SO₃, d. 1.84 800 Weight of CH3COC2H5 used 160 400 800 Raw oil obtained 150 315 510 446

It should be noted in connection with these tables of fractionation that the intermediate fractions, indicated in the table only by a temperature interval, many times represent nearly constant-boiling mixtures. These could be only partially separated even after repeated fractionation. The investigators' of the products of condensation of acetone encountered the same difficulty. That these fractions were truly "constant-boiling mixtures" was shown also by the fact that the refractive index varied, and that the combustion data on them varied.

Homomesityl Oxide

Physical Constants.—Homomesityl oxide, $C_8H_{14}O$, is a nearly colorless liquid with a peppermint-like odor and a camphor-like taste; b. p., $156-160^{\circ}(625 \text{ mm.})$; d_4^{20} , 0.8628; n_D^{20} , 1.4453; $M_D \longrightarrow 38.94$ (calc., 38.72); mol. wt. (from the vapor density), calc., 126.15; found, 132, 131.

Analysis. Calc. for C₈H₁₄O: C, 76.13; H, 11.18. Found: C, 76.35; H, 11.39.

Preparation of a Liquid Oxime.—The oxime was prepared by allowing the ketone to react with free hydroxylamine under the supposition that a crystalline oxime would in that way be formed as is the case with mesityl oxide; 20 g. of oil was dissolved in 70 cc. of alcohol and a saturated water solution of the calculated amount of hydroxylamine hydrochloride was added gradually. More alcohol was added to make the solution clear. The mixture was then refluxed for 2 hours, which caused a blackening of the product. A few drops were placed on a microscope slide and allowed to evaporate. No crystals appeared. The reaction mixture was, therefore, allowed to stand for 10 days. A saturated solution of potassium carbonate was then added gradually, causing the separation of an oily layer in which a few crystals were suspended. Since all attempts to cause further crystallization failed, the product was distilled at 17 mm. This

⁷ Ref. 2g, p. 212.

distillation gave 10 g. of the original oil and a fraction boiling at 120-140°. By repeated distillation a constant-boiling fraction was obtained of light greenish tinge, boiling at 132-137° (17 mm.).

Analysis. Calc. for C₈H₁₄NOH: N, 9.9. Found (Kjeldahl): 9.2.

An Attempt to Prepare a Semicarbazone.—Bodroux and Taboury⁸ report a semicarbazone of homomesityl oxide melting at 114–115°. We wish to call attention to the fact that, although we also obtained a crystalline precipitate of melting point 114–115° by the action of 1 molecule of homomesityl oxide on 1 molecule of semicarbazide in alcoholic solution using potassium acetate to neutralize the semicarbazide hydrochloride, this precipitate proved to be a mixture. The precipitate was dissolved in alcohol and diluted with an equal volume of water. A fraction of melting point 140° precipitated almost immediately. The remaining fraction melted at 108°. The authors believe the reaction to be more complex than indicated by the work of Bodroux and Taboury, and hope by further work to isolate the normal semicarbazone of homomesityl oxide and a pyrazoline derivative which seems to be formed.

The Semicarbazide-semicarbazone.—One molecule of homomesityl oxide was allowed to react with 2 molecules of semicarbazide hydrochloride in alcoholic solution. In an acid solution of this kind the semicarbazide-semicarbazone precipitated almost immediately. The crystals were insoluble in alcohol and water and ordinary organic solvents. They were soluble in hot dil. hydrochloric acid and were reprecipitated by neutralizing the acid with sodium hydroxide. By recrystallizing in this way they were obtained pure, appearing as microscopic prisms; m. p., 265–266° (decomp.).

Analysis. Calc. for C₁₀H₂₂N₆O₂: N, 32.55. Found (Kjeldahl): 32.6.

Oxidation with Potassium Permanganate.—Twenty-five g. of homomesityl oxide was shaken with 600 cc. of water, in 50g. portions. A 5% solution of potassium permanganate was added in small quantities and the mixture frequently and vigorously shaken until it retained the color after standing for 24 hours. The slight excess of permanganate was destroyed by heat. A little over 2 molecules of permanganate were required to 1 of homomesityl oxide. The large volume of solution thus obtained was evaporated to 400 cc. and the residue was then acidified with dil. sulfuric acid. Carbon dioxide was evolved in this step. The acid solution was extracted several times with ether. After being dried over anhydrous sodium sulfate, the ether solution was evaporated, leaving a brown liquid. This liquid was distilled at 15 mm. A study of the analytical results of the distillate shows that the liquid was a mixture of propionic acid and some lower-boiling substance, not acetic acid. Three fractions were obtained. The highest one on titration was shown to be propionic acid; 0.2801 g. required for neutralization 0.1485 g. of sodium hydroxide solution, a quantity which neutralizes 0.2784 g. of propionic acid.

The next lower fraction could not have been acetic acid and it could not have contained acetic acid, since 0.4926 g. required for neutralization 0.2454 g. of alkali solution, a quantity that neutralizes 0.4601 g. of propionic acid, and only 0.3681 g. of acetic acid. Moreover, the highest fraction, b. p., $45-50^{\circ}$ (15 mm.), gave a propionyl p-toluidine melting at 118° (the pure crystals should melt at 123°; not enough was obtained to be recrystallized); also, the boiling point of the fraction was 125-133° (622 mm.), identical with that of a known pure propionic acid at Boulder. A special effort was made to isolate acetic acid from these products; none was found. The presence of methylethyl ketone in the lowest distillate was indicated by the odor, but owing to the small yield of oxidation products, methylethyl ketone could not be isolated. The course of the reaction evidently is (C_2H_5) (CH₃)C=CH.CO.C₂H₅ + 4O = (C_2H_5) (CH₃)C=O + C_2H_5

⁸ Bodroux and Taboury, Compt. rend., 149, 422 (1909).

COOH + CO₂, and we must conclude that the homomesityl oxide here obtained has the constitution (C_2H_6) (CH₂) C=CH.CO.C₂H₅.

Homophorone

Physical Constants.—Homophorone, $C_{12}H_{20}O$, is a clear, slightly straw-colored liquid with a camphor-like odor and taste; b. p., $206-210^{\circ}$ (625 mm.); d_4^{20} , 0.8857; n_D^{20} , 1.4792, M_D , calc. (without exaltation), 56.71; + exaltation for phorone (+3) = 59.71; found; 57.72; mol. wt. (from vapor density), calc., 180.22; found, 185, 172.

Analysis. Calc. for C12H20O: C, 79.93; H, 11.18. Found: C, 79.59; H, 10.97.

The composition of this compound must be determined by further work as indicated in the discussion. Moreover, the data given above are from a fraction prepared by condensing methylethyl ketone with sulfuric acid. It is believed to be present among the products obtained by the action of sodium ethylate. An unexpected difficulty, however, was encountered in getting a pure fraction and none has been obtained so far. The authors propose to continue the work on this point.

The Homo-isophorones, C12H20O

Homo-isophorone, b. p. 256-260° (630 mm.).—This homo-isophorone is a clear yellow liquid with a weak odor and taste of terpene; $d_{\rm p}^{20}$, 0.9492; $n_{\rm p}^{20}$, 1.5045; $M_{\rm p}$, calc. (Eisenlohr), 54.98 + exaltation for isophorone, 54.98 + 1.1 = 56.08; found, 56.12; mol. wt. (from vapor density), calc., 180.22; found, 178,188.

Analysis. Calc. for C₁₂H₂₀O: C, 79.93; H, 11.18. Found: C, 80.08; H, 11.12.

An attempt was made to duplicate the work of Braun and Kittel⁶ who reported that this homo-isophorone adds 4 atoms of bromine. We were unable to verify their results since our investigations showed that hydrogen bromide was generated in large volume long before an amount of bromine corresponding to 2 atoms was added. The addition of hydrogen chloride was then investigated; 5 g. of the oil was dissolved in 20 cc. of dry liquid carbon disulfide, and hydrogen chloride, dried over phosphorus pentoxide, was passed through the solution. A heavy, black oil separated. It was carefully removed with a pipet and the solvent allowed to evaporate. A weighed amount was then refluxed with a standard solution of sodium hydroxide, and the excess alkali was titrated with 0.1 N acid; 0.3898 g. of substance contained 0.0641 g. of hydrogen chloride. This result indicates that this homo-isophorone contains but one double bond and not two as reported by Braun and Kittel.

Homo-isophorone, b. p. $280-285^{\circ}$ (630 mm.).—This homo-isophorone is a golden-brown, slightly viscous liquid. Its odor and taste are camphor-like; d_{2}^{40} , 0.9693; n_{D}^{20} , 1.5115; M_{D} , calc., 54.98 + exaltation for isophorone = 56.08; found, 55.74; mol. wt. from vapor density, calc., 180.22; found, 179, 168.

Analysis. Calc. for C12H20O: C, 79.93; H, 11.18. Found: C, 80.28; H, 10.81.

The Synthesis of the γ - and δ -Homo-isophorones

In this procedure the method of Knoevenagel^{2h} was followed. First, methyl aceto-acetic ester was prepared by the usual method; a pure product was obtained; b. p., 176-178° (630 mm.). Fifty g. of the experimentally obtained homomesityl oxide was mixed with the calculated amount (57 g.) of methyl aceto-acetic ester, and the mixture well cooled. A 25% solution of sodium ethylate in absolute alcohol was prepared and enough of the reagent used to furnish sodium in the proportion 1 Na: 1 CH₂COCHCH₃.-COOC₂H₅. The alcoholate solution was allowed to stand for 9 days at a temperature of 5-10°, then refluxed on the water-bath for 5 hours to complete the reaction, made acid with 20% sulfuric acid and refluxed for 6 hours to saponify the condensation

product. The solution was then cooled and washed 5 times with ether. The ether solution was made slightly alkaline by washing with dil. sodium hydroxide solution, and dried with anhydrous sodium sulfate. After the ether had been distilled, there remained about 50 g. of an oil. Much of the original homomesityl oxide was recovered from this product. The following fractions were obtained from the oil which bore every resemblance to the 2 homo-isophorones described above, in color, odor, taste and physical constants.

Fraction 1: b. p., $145-165^{\circ}$ (15 mm.); n_D^{20} , 1.4970. The corresponding pure homo-isophorone: b. p., $256-260^{\circ}$ (630 mm.); b. p., $150-157^{\circ}$ (15 mm.); n_D^{20} , 1.5045.

Fraction 2: b. p., $165-180^{\circ}$ (15 mm.); n_D^{20} , 1.5053. The corresponding pure homoisophorone: b. p., $280-285^{\circ}$ (630 mm.); b. p., $170-178^{\circ}$ (15 mm.); n_D^{20} , 1.5115.

It is evident, therefore, that the two higher-boiling compounds obtained by the condensation of methylethyl ketone have the constitutions γ and δ or δ and γ , as developed in the discussion.

Summary

- 1. The condensation products of methylethyl ketone under the influence of hydrogen chloride, of sulfuric acid, and of sodium ethylate have been studied. Hydrogen chloride yields 2 products, homomesityl oxide and homophorone. Both sulfuric acid and sodium ethylate yield homomesityl oxide, homophorone, and 2 homo-isophorones, besides other high-boiling products whose nature has not yet been determined.
- 2. Homomesityl oxide, prepared with the above reagents, has been shown to have the constitution $(C_2H_5)(CH_3)C=CH.CO.C_2H_5$.
 - 3. A liquid oxime of homomesityl oxide has been prepared.
- 4. The semicarbazone of homomesityl oxide reported by Bodroux and Taboury has been shown to be a mixture. The semicarbazide-semicarbazone of mesityl oxide has been prepared.
 - 5. The probable constitution of homophorone has been discussed.
- 6. Two homo-isophorones have been isolated, their important constants determined, and their structures shown to correspond to one of two possible constitutional formulas, γ and δ as shown above.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY]

THE STRUCTURE OF PHENOLPHTHALEIN OXIME

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Two formulas (I and II) have been proposed for phenolphthalein oxime since it has been shown that Formula III proposed by Friedländer

is incorrect.

In order to explain the quantitative decomposition of the oxime by dil. sulfuric acid into p-hydroxybenzoyl-o-benzoic acid and p-aminophenol, Orndorff and Murray assume Formula I for the compound. They further assume that phenolphthalein oxime, like the oximes of the ketones, undergoes the Beckmann rearrangement giving an intermediate product which is the p-hydroxyanilide of p-hydroxybenzoyl-o-benzoic acid.

This intermediate product or its ketone form then hydrolyzes into *p*-hydroxybenzoyl-*o*-benzoic acid and *p*-aminophenol.

$$HOC_6H_4-C=O$$

 $C_6H_4CONHC_6H_4OH$
 $+ HOH =$
 $HO-C_6H_4-C=O$
 $+ H_2N-C_6H_4OH$

The fact that p-hydroxyphthalanil is obtained when an excess of hydroxylamine is used in the preparation of the oxime or as H. Meyer² found by heating the oxime with a solution of hydroxylamine hydrochloride is also

¹ See R. Meyer and Kissen, *Ber.*, **42**, 2825 (1909), and Orndorff and Murray, This Journal, **39**, 689 (1917).

² Meyer, Monaish., 20, 346 (1899).

explained by assuming the formation of the intermediate product which then breaks down into p-hydroxyphthalanil and phenol.

Intermediate product

p-Hydroxyphthalanil

Pheno1

The reduction product of phenolphthalein oxime which H. Meyer and R. Meyer have shown to have the structure

HOC₆H₄—C—H

C₆H₄—NC₆H₄OH(
$$p$$
)

is also formed according to Orndorff and Murray not from the oxime but from the intermediate product.

It will be seen from the foregoing that it would be highly desirable to prove that phenolphthalein oxime undergoes the Beckmann rearrangement like the ketoximes, to isolate the intermediate product and show that it undergoes the above changes. The present paper shows how this was accomplished.

Experimental Part

R. Meyer and Kissen¹ have prepared what they call a triacetate of the oxime by heating it with acetic anhydride and sodium acetate. As this substance is *colorless*, whereas the oxime is *yellow*, it was thought that it might be the triacetate of the intermediate product and that when the oxime is acetylated it undergoes the Beckmann rearrangement. If this is true then it seemed quite likely that on saponification the triacetate would give the intermediate product and not the oxime. Experiment showed that this idea was correct.

Triacetate of the p-Hydroxyanilide of p-Hydroxybenzoyl-o-benzoic Acid.—This was made from the oxime by the method given by R. Meyer and Kissen¹ and carefully purified by recrystallization from acetone. It crystallized in colorless needles that melted at 235°. R. Meyer and Kissen give the melting point of their product as 229–230°. Analyses on the product dried in a vacuum desiccator over concd. sulfuric acid gave the following results:

Analyses. Subs., 0.2388, 0.2238: CO_2 , 0.5939, 0.5568; H_2O , 0.1010, 0.0940. Calc. for $C_{26}H_{21}O_7N$: C, 67.95; H, 4.61. Found: C, 67.82, 67.85; H, 4.73, 4.70.

Subs., 1.0267, 1.0500: cc. of 0.1 N H_2SO_4 , 23.14, 23.53. Calc. for $C_{26}H_{21}O_7N$: N, 3.05. Found: 3.16, 3.14.

Subs., 0.5004: 32.62 cc. of 0.1 N NaOH. Calç. for $C_{26}H_{12}O_4N(COCH_3)_2$: CH_3CO , 28.11. Found: 28.10.

In view of the statement of H. Meyer³ that there are at least 3 triacetates of the oxime, all insoluble in alkali and that he had already obtained 2 of them in pure form and

³ H. Meyer, Monatsh., 17, 440 (1896).

had analyzed them, the crude acetate was subjected to careful fractional crystallization. Only the triacetate melting at 235° was obtained.

Saponification of the Triacetate by Sulfuric Acid. The Intermediate Product.—The triacetate is saponified in the cold by conc. sulfuric acid. A dark red, viscous solution was formed. This was gradually poured into crushed ice, the solution was vigorously stirred and finally diluted with a great amount of water, filtered and allowed to stand. A yellow crystalline powder settled. This was freed from sulfuric acid by dissolving it in a cold 4% solution of sodium hydroxide and reprecipitating it with a slight excess of very dilute hydrochloric acid. The colorless precipitate after being washed with water was boiled with water. It first melted, then solidified and finally all passed into solution on boiling with sufficient water. As the solution cooled, small colorless, flaky crystals formed that melted at 135° with decomposition. The substance loses very little weight in a vacuum desiccator. The substance dried in a desiccator gave the following results on analysis.

Analyses. Subs., 0.2908, 0.2995, 0.2961: CO₂, 0.7110, 0.7324, 0.7246. H₂O, 0.1334, 0.1366, 0.1358. Subs., 1.0010, 1.0007: cc. of 0.1 N H₂SO₄, 28.2, 28.0. Calc. for C₂₀H₁₂-ON(OH)₃ + 1¹/₂H₂O: C, 66.65; H, 5.04; N, 3.89. Found: C, 66.68, 66.69, 66.74; H, 5.13, 5.10, 5.13; N, 3.92, 3.92.

The above results show that the substance is the *p*-hydroxyanilide of *p*-hydroxybenzoyl-*o*-benzoic acid with 1.5 molecules of water of crystallization. An attempt was made to determine the water of crystallization by heating the substance in an atmosphere of carbon dioxide at 95°. Water vapor was given off and the substance melted to a dark red liquid which solidified on cooling to a dark red glass; 0.4892 g. of substance lost 0.0639 g. of water after 6 hours' heating; the calculated loss for 2.5 molecules of water is 0.0640 g. Thus, the intermediate product when heated not only loses all its water of crystallization but also an additional molecule of water of constitution as shown in the following equation.

$$C_6H_4OH$$
 $C=C_6H_4=O$
 $C=C_6H_4=O$
 $C=C_6H_4=O$
 $C=C_6H_4=O$
 $C=C_6H_4OH + 2^1/2H_2O$
 $C=C_6H_4OH + 2^1/2H_2O$

An attempt made to convert the red glass into the intermediate product by boiling it with water was unsuccessful. The red compound is very difficultly soluble in hot water and only after prolonged boiling with water imparts a faint pink color to it. It is very soluble in dilute solutions of alkalies, giving a dark green solution. When this alkaline solution is acidified a yellow amorphous precipitate is formed. An attempt was also made to get the intermediate product in the anhydrous form by recrystallizing it from boiling water. The product, however, had the same melting point and on heating lost the same amount of water (i. e., 2.5 molecular equivalents) as before.

The action of organic solvents on the intermediate product is very remarkable. Acetone, ethyl alcohol, methyl alcohol, or ethyl acetate dis-

solves it readily and the recrystallized product from each of these solvents has a different melting point. That from acetone melts at $94-95^{\circ}$, from methyl alcohol at 125° , from ethyl alcohol at 130° and from ethyl acetate at $195-198^{\circ}$. The intermediate product is slightly soluble in hot benzene or in hot toluene and insoluble in ether, ligroin, chloroform or carbon tetrachloride. The product crystallized from ethyl acetate seems to have the formula $C_{20}H_{12}ON(OH)_3 + \frac{1}{2}CH_3COOC_2H_5$ from the analysis.

Analysis. Subs., 0.6675: 19.11 cc. of 0.1 N H₂SO₄. Calc. for $C_{20}H_{12}ON(OH)_3 + \frac{1}{2}CH_3COOC_2H_5$: N, 3.92. Found: 4.01.

Subs., 0.3230. Calc. loss for $H_2O+{}^1/_2CH_3COOC_2H_5$: 0.0543 g. Loss after heating for 5 hours at 95°, 0.0540 g.

The odor of ethyl acetate was detected during the heating and a red glass was left in the boat.

Saponification of the Triacetate by Alkali.-Twenty g. of the triacetate, made from the oxime, was treated with 200 cc. of a 4% solution of sodium hydroxide. All of it dissolved in the cold after the solution stood a few hours and was shaken occasionally. The solution was colored yellow. If allowed to stand for a few days, it becomes green. The yellow solution was acidified with dil. hydrochloric acid and a white flocculent precipitate was obtained. This was collected on a filter, washed and boiled with a large amount of water. It acted exactly like the intermediate product obtained from the triacetate by saponification with conc. sulfuric acid. It first melted under the water, then solidified and finally all went into solution on boiling it with sufficient water. The crystals obtained from this solution on cooling were identical with those of the intermediate product made by saponification of the triacetate with concd. sulfuric acid and had the same m. p. The substance also gave the same reduction product, the same p-hydroxyphthalanil, the same dibenzoate, the same triacetate and the same trimethyl ether as the intermediate product made from the triacetate by saponification with concd. sulfuric acid. There is no doubt of the identity of the 2 products. This method of saponification of the triacetate gives a quantitative yield of the intermediate product and is better than the one with concd. sulfuric acid. The intermediate product made in this way also lost the same amount of water when heated and gave a red glass $(0.4832 \text{ g. lost } 0.0606 \text{ g. after 6 hours at } 92^{\circ}; \text{ calc. for } 2^{1}/_{2} \text{ mols. of } H_{2}O, 0.0603 \text{ g.}).$

Hydrolysis of the Intermediate Product with Dilute Sulfuric Acid.—On boiling the intermediate product with dil. sulfuric acid (1:8), it is hydrolyzed to p-hydroxy-benzoyl-o-benzoic acid and p-aminophenol just as the oxime is. A quantitative determination resulted as follows: 1.0037 g. of substance gave 0.5759 g. of p-hydroxybenzoyl-o-benzoic acid and 0.2883 g. of p-aminophenol. The calculated amounts are p-hydroxybenzoyl-o-benzoic acid, 0.6187 g.; p-aminophenol, 0.3039 g.

Decomposition of the Intermediate Product with Hydroxylamine Hydroxylamine Hydroxylamine hydroxylamine hydrochloride. After a short time, long colorless needles separated. These were recrystallized from dil. alcohol and found to melt at 288° with decomposition—as in the case of p-hydroxyphthalanil obtained from the oxime by the same treatment. A qualitative test for phenol, the other product of the decomposition, was also obtained. A Kjeldahl analysis of the product melting at 288° showed that it was p-hydroxyphthalanil.

Analysis. Subs., 0.3370: cc. of 0.1 N H₂SO₄, 14.14. Calc. for C₂₄H₉O₂N: N, 5.86. Found: 5.88.

Reduction of the Intermediate Product.—Five g. of the intermediate product was dissolved in about 60 cc. of dil. alcohol and 5 cc. of coned. sulfuric acid. Zinc dust was

then added and the mixture carefully heated. The red color of the solution gradually faded to a light yellow. The zinc was then filtered off and the filtrate poured into water. The white precipitate obtained was recrystallized from dil. alcohol and found to melt at 256°—the same melting point as that of the reduction product made from the oxime by the same method. A mixture of the two products melted sharply at the same temperature. An acetyl derivative of the reduction product was also made, m. p., 205–208°, the melting point given by Herzig and H. Meyer for the diacetate of the reduction product.

Acetylation of the Intermediate Product.—Acetylation of the intermediate product with acetic anhydride and sodium acetate gave the same triacetate as was obtained from the oxime.

The product crystallized from acetone had the same melting point, and the same chemical and physical properties as the triacetate made from the oxime. Kjeldahl analyses on the substance dried in a desiccator also showed that it was identical with the triacetate made from the oxime.

Analyses. Subs., 0.9522, 0.9647: cc. of 0.1 N H_2SO_4 , 20.86, 21.30. Calc. for $C_{26}H_{21}O_7N$: N, 3.05. Found: 3.07, 3.09.

Benzoylation of the Intermediate Product.—R. Meyer and Kissen¹ made what they call a tribenzoate of the oxime by benzoylating the oxime by the Schotten-Baumann reaction. It was thought that this benzoate might be the benzoate of the intermediate product, as in the case of the triacetate made from the oxime.

Ten g. of the intermediate product was dissolved in 150 cc. of 20% sodium hydroxide solution and an excess of benzoyl chloride was added, a little at a time while the mixture was shaken vigorously. A white precipitate was formed. It was washed with a dilute solution of sodium hydroxide, boiled with water to remove benzoic acid and then recrystallized from methyl alcohol. It melted at 227° and the melting point did not change when the substance was recrystallized from ethyl alcohol and from acetone. R. Meyer and Kissen give the melting point of their tribenzoate as 175°. Kjeldahl determinations of the substance dried in a desiccator gave the following results.

Analyses. Subs., 0.7828, 0.7815: cc. of 0.1 N H_2SO_4 , 14.70, 15.09. Calc. for $C_{20}H_{13}O_4N(COC_6H_5)_2$: N, 2.59. Found: 2.63, 2.70.

This indicates that the substance is a dibenzoate instead of a tribenzoate. Further evidence of this was secured from the results of combustion analyses.

Analyses. Subs., 0.2994, 0.3095: CO₂, 0.8259, 0.8536; H₂O, 0.1158, 0.1228. Calc. for $C_{20}H_{18}O_4N(COC_6H_6)_2$: C, 75.39; H, 4.28. Found: C, 75.23, 75.21. H, 4.33, 4.44.

An attempt was made to obtain a mono-acetate of this dibenzoate by boiling it with acetic anhydride but the product was the triacetate of the intermediate product.

Benzoylation of Phenolphthalein Oxime.—Meyer and Kissen's experiment was repeated using exactly the same quantity of materials that they specify. The same dibenzoate was obtained as in benzoylating the intermediate product. It melted at 227° and gave the following results on analysis.

Analyses. Subs., 0.4112, 0.4042: cc. of 0.1 N H_2SO_4 , 7.45, 7.64. Calc. for $C_{20}H_{13}$ - $O_4N(COC_6H_6)_2$: N, 2.59. Found: 2.54, 2.65.

Subs., 0.3143: CO₂, 0.8679; H_2O , 0.1208. Calc. for $C_{20}H_{13}O_4N(COC_6H_6)_2$: C, 75.39; H, 4.28. Found: C, 75.31; H, 4.30.

Repeated attempts to make the tribenzoate described by Meyer and Kissen were unsuccessful.

It will be seen from these results that when the oxime is acetylated and benzoylated, it undergoes the Beckmann rearrangement and gives the triacetate and the dibenzoate of the intermediate product. These have the following structural formulas.

$$\begin{array}{cccc} CH_{\circ}COOC_{\circ}H_{4}-C-OCOCH_{\circ} & C_{\circ}H_{\circ}COOC_{\circ}H_{4}-C-OH \\ C_{\circ}H_{4} & NC_{\circ}H_{4}OCOCH_{\circ} & C_{\circ}H_{\bullet} & NC_{\circ}H_{4}OCOC_{\circ}H_{4} \\ \hline C=O & C=O & Dibenzoate \\ \end{array}$$

Methylation of the Intermediate Product.—R. Meyer and Spengler⁴ have made the trimethyl ether of phenolphthalein oxime by methylating it in alkaline solution with dimethyl sulfate. As they describe this ether as almost colorless, it was thought that it might be the trimethyl ether of the intermediate product.

Five g. of the intermediate product was dissolved in 60 cc. of 30% of sodium hydroxide solution in a stoppered flask and an excess of dimethyl sulfate gradually added with vigorous shaking. The reaction soon took place with the evolution of heat and a white solid separated. This was collected, washed with water and recrystallized from methyl alcohol. The melting point of the recrystallized product was found to be 131–133°. Meyer and Spengler give the melting point of the trimethyl ether of the oxime as 145–146°. Phenolphthalein oxime was therefore methylated with dimethyl sulfate by the method given by Meyer and Spengler. The melting point of the ether recrystallized from both methyl alcohol and acetone was 145–146°; but the crystals are distinctly yellow, while those of the ether made from the intermediate product are colorless. Kjeldahl analyses were made on both substances and the results show that both are trimethyl ethers.

Analyses. (1) Trimethyl ether of the intermediate product. Subs., 0.5182, 0.5154: cc. of 0.1 N H₂SO₄, 13.33, 13.62. Calc. for C₂₀H₁₂ON(OCH₃)₃: N, 3.73. Found: 3.60, 3.70.

(2) Trimethyl ether of the oxime (yellow). Subs., 0.5150: cc. of 0.1 N $\rm H_2SO_4$, 13.91. Calc. for $\rm C_{20}H_{12}ON(OCH_3)_3$: N, 3.73. Found: 3.78.

It will be seen from these results that the 2 ethers are isomeric and that the oxime does not undergo the Beckmann rearrangement when methylated in alkaline solution with dimethyl sulfate. The structures of the two compounds are represented as follows.

Trimethyl ether of the oxime Trimethyl ether of the intermediate product

Synthesis of the Intermediate Product.—H. Meyer and R. Meyer have both made the reduction product of the oxime synthetically by heating p-hydroxy-phenylphthalide with p-aminophenol.

⁴ R. Meyer and Spengler, Ber., 36, 2964 (1903).

It was thought that p-hydroxybenzoyl-o-benzoic acid and p-aminophenol might react in a similar manner.

Eleven g. of p-hydroxybenzoyl-o-benzoic acid and 5 g. of p-aminophenol were melted together. Instead of obtaining the intermediate product, a dark purple solid resulted. It was very sparingly soluble in hot water, and colored the solution pink only after prolonged boiling. It is readily soluble in solutions of the alkalies giving a deep purple solution from which it is precipitated by acids. It is probably a mixed phthalein.

The results given in this paper can only be explained by assuming that phenolphthalein oxime has a structure similar to that of phenolphthalein imide and phenolphthalein anilide, substances formed from phenolphthalein and ammonia or from phenolphthalein and aniline, just as the oxime is formed from phenolphthalein and hydroxylamine.

That these two substances do not undergo reduction or hydrolysis as readily as the oxime is easily explained because they do not undergo the Beckmann rearrangement as the oxime does. It is the intermediate product formed by the Beckmann rearrangement of the oxime that in reality undergoes the reduction and the hydrolysis. The objection that has been made to this formula by R. Meyer that it does not explain the color of the compound may be answered by calling attention to the fact that although phenolphthalein is a colorless substance to the naked eye, it has two absorption bands in the ultraviolet. Phenolphthalein oxime also has two absorption bands in the ultraviolet and apparently the effect of substituting the <NOH group for oxygen is the shifting of one of these bands towards the visible part of the spectrum. A small part of the blue is cut out and hence the solution appears yellow to the eye. Attention should also be called to the fact that phenolphthalein oxime, like the imide and anilide of phenolphthalein, dissolves in solutions of alkalies without under-

going the change into the quinoid condition so characteristic of phenol-phthalein.

Summary

The results obtained in this work may be briefly summarized as follows.

- 1. It has been shown that phenolphthalein oxime undergoes the Beckmann rearrangement when acetylated or benzoylated. The triacetate and dibenzoate formed are derivatives of the *p*-hydroxyanilide of *p*-hydroxybenzoyl-*o*-benzoic acid and not of the oxime.
- 2. The intermediate product (p-hydroxyanilide of p-hydroxybenzoyl-o-benzoic acid) has been isolated by saponification of its triacetate made from the oxime both with sulfuric acid and with dilute solutions of the alkalies.
- 3. It has been shown that the intermediate product undergoes hydrolysis when heated with dil. sulfuric acid, just as the oxime does, into p-hydroxybenzoyl-o-benzoic acid and p-aminophenol and the yield of both products is practically quantitative.
- 4. When reduced with zinc dust and dil. sulfuric acid the intermediate product gives the same reduction product that the oxime does.
- 5. When heated with a solution of hydroxylamine hydrochloride the intermediate product gives p-hydroxyphthalanil and phenol just as the oxime does.
- 6. When acetylated the intermediate product gives the same triacetate that is formed when the oxime is acetylated.
- 7. When benzoylated by the Schotten-Baumann reaction the intermediate product gives a dibenzoate, identical with that obtained from the oxime by the same treatment. Attempts to make the tribenzoate of the oxime described by R. Meyer and Kissen were unsuccessful.
- 8. The intermediate product gives a *colorless* trimethyl ether, when methylated in alkaline solution with dimethyl sulfate, isomeric with the *yellow* trimethyl ether obtained from the oxime by the same treatment.
- 9. Attempts to make the intermediate product synthetically from p-hydroxybenzoyl-o-benzoic acid and p-aminophenol were unsuccessful. A mixed phthalein was obtained instead.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MAINE]

CHARACTERISTICS OF THE TWO CRYSTALLINE FORMS OF GLYCINE

By C. A. Brautlecht and N. F. Eberman Received April 9, 1923

Emil Fischer¹ observed that the needle-shaped form of glycine, precipitated from water solution by absolute alcohol, reacts smoothly with phosphorus pentachloride in presence of acetyl chloride to form the hydrochloride of glycyl chloride (amino-acetyl chloride). The plate form, prepared by evaporating the water solution and drying at 100°, did not react in the same manner. Fischer believed that this behavior had to do with isomerism. There are only two structures for glycine theoretically possible, the straight chain (NH₂CH₂COOH) and the inner salt NH₃CH₂COO. There is much controversy concerning the correct form

and much additional experimentation is needed before a satisfactory conclusion can be reached.

Falk and Sugiura² studied the two forms of glycine and observed that the needle form began to decompose at a slightly higher temperature than the plate; that the time interval after solution of the plate form caused a slight difference in amino nitrogen content by the Van Slyke method, whereas the needle form underwent no change; and that the plate form took up about one atomic proportion of bromine while the needle form took up about two, the bromine, however, leaving the glycine readily. Their conclusion was that a difference existed between the two forms.

H. Biltz and H. Paetzold³ observed that the two forms of glycine did not react with diazomethane in the absence of moisture. When moisture was present, both forms acted exactly alike, yielding betaine hydrochloride. When the two forms were pulverized and dried at 130° both plates and needles decomposed at the same temperature and in the same manner. They believed that the difference noted by Falk and Sugiura in decomposition temperature for the two forms, a fact confirmed by them when the crystals were dried at 100–103°, was due to the plates occluding mother liquor which depressed the decomposition temperature. Biltz and Paetzold then repeated the bromination experiments of Falk and Sugiura and observed that bromine taken up by both forms was lost on standing in a vacuum desiccator over moist potassium hydroxide; that each form took up about the same quantity of bromine which was adsorbed or loosely attached and variable in quantity in different experiments and was not affected whether the glycine was strongly dried or not. In repeating E.

¹ Fischer, Ber., 38, 2914 (1905).

² Falk and Sugiura, J. Biol. Chem., 34, 29 (1918).

³ Biltz and Paetzold, Ber., 55, 1066 (1922).

Fischer's acetylation experiments,¹ they obtained similar results with both forms when dried at 130°, whereas when the substances were dried at 100° the results agreed with those of Fischer, the needles reacting to form the glycyl chloride hydrochloride in about 50% yield, whereas the plates reacted only to a slight extent. It thus becomes possible to obtain this acid chloride from glycine in plate form, prepared by evaporation of the water solution, by heating to 130° for 9 hours or possibly less. The questions then arise, since the supposition can be made that the needle form has the open structure, (1) does the action of heat at 130° effect a transformation of the plate form into the needle form; (2) does solution or drying at 130° effect an equilibrium between the two forms; (3) does glycine in crystalline forms and in the presence of water have a different structure? We hope to furnish a little evidence from the following experiments to aid in answering these questions.

Experimental Part

The two forms of glycine were prepared as described by Fischer¹ from imported glycine and glycine prepared according to the method of Klages, ⁴ T. Curtius and E. Welde⁵ and K. Kraut.⁶ The material was pulverized, sifted, and dried at 100–103°. Photomicrographs of the plate and needle forms before pulverization indicated that there was water of occlusion in the plates at times. The processes of pulverizing and drying at 100–103° and sifting to 0.3 mm. mesh apparently remove this water.

Decomposition Temperature of the Two Forms

From the following and similar results, using a long thermometer, it appears that there is no difference in decomposition temperature between the two forms.

Appearance	•	Needl		ecomposi ate form °C.	Ne and	edle plates	Ne	edle olate	form form form 90 rat	and
Light brown		2	28	228	2	27			224	9.35
Dark brown		2	29	229	2	28			228	
Black spots		2	30	230	2	30			229	
Decomp., gas formed		2	33	233	2	33			233	

Content of Moisture or Alcohol

Although Fischer¹ in his experiments on the action of phosphorus pentachloride and acetyl chloride, carefully dried each form similarly at 103° and although Falk and Sugiura² also first dried the 2 forms of glycine, it appeared desirable to determine the amounts of moisture present in the airdry material since, as will be shown, the presence of moisture has an effect upon the degree and intensity of the reaction.

- ⁴ Klages, Ber., 36, 1507 (1903).
- ⁵ Curtius and Welde, ibid., 43, 868 (1910).
- ⁶ Kraut, Ann., 266, 295 (1891).

The two forms were prepared as usual, ground uniformly, in dried air and the moisture was determined by heating at 100°, and cooling in a desiccator.

	Needles		Plates			
Sample G.	Loss in weight G.	%	Sample G.	Loss i G.	n weigh	ıt %
1.0308	0.0036	0.34	1.9878	0.0076	(0.38
1.7547	.0034	.19	1.9243	.0060		.31
1.0291	.0005	05	1.0314	.0015		.13
0.9164	.0010	.10	0.9435	.0013		.16
.1756	.0010	.57	.2093	.0008		.38
.1774	.0011	.62	.2525	.0009		.35
	Av	31			Av.	.28

In one experiment, after pulverized plates and needles had been dried over phosphorus pentoxide for 24 hours, the plates lost 0.05% in weight at 100° in 24 hours, and the needles lost 0.20% under the same conditions. From these results it appears that the small quantity of moisture or alcohol held by the air-dry glycine is the same for both forms.

Action of Hydrogen Chloride

Dry hydrogen chloride was passed over each of the two powdered forms of glycine after it had been sieved to 0.3 mm. mesh, and dried at 100°. Bell jars were used with a tray of fused calcium chloride at the bottom. Before removing the samples for weighing, the bell jar was first swept out with dry air, or the treated glycine was placed in a vacuum desiccator.

		Glycine needles		
	~Wei	ght	Glycine hyd	rochloride
Sample G.	After 3 days	After 6 days	Calc. G.	Found %
0.1336	• • •	0.1386	0.1985	69.7
.1210	• • •	.1264	.1790	70.6
.1112	0.1160	.1190	.1648	72.2
.5000	.7408		.7425	99.7
	•	Glycine plates		
1270	.1368	.1462	.1880	77.8
.1265	.1356	.1456	.1874	77.7
.1052	.1085	.1115	.1556	71.7
$.5000^{a}$.7040		.7425	84.0

[&]quot;In this experiment the dried gas was conducted over the powdered crystals in fractions, allowed to remain in contact during the intervals and then the excess removed in a vacuum desiccator. The results of this series show that dry hydrogen chloride acts slowly on dry glycine in either form.

In the presence of moisture, for instance, when glycine was treated with hydrogen chloride in a bell jar with a dish of water present the hydrochloride was more easily and completely formed. The samples were dried at 100° after the reaction, before weighing.

The results expressed in the last tabulation show that moisture permits hydrogen chloride to react quantitatively with glycine in 6 days. It is

•	Needl	les	
		Glycine hyd	
Sample G.	Weight after 6 days	Cale. G.	Found %
0.1045	0.1528	0.1547	98.77
.1071	.1550	.1585	97.79
.1139	.1675	. 1687	99.30
.1077	. 1546	. 1595	96.90
	Plate	es	
.1122	.1611	. 1611	100.00
.1150	.1693	.1704	99.35
.1093	.1556	.1618	96.20
.1305	.1907	. 1932	98.60

also apparent that no difference exists between the two forms chemically, in the presence of moisture.

Action of Sulfur Dioxide

Sulfur dioxide was allowed to react with the two forms. They were first exposed in a jar under ordinary moisture, temperature and pressure conditions. Here the reaction proceeds according to the equation: $2CH_2(NH_2)COOH + H_2SO_3 \longrightarrow (CH_2.NH_2.COOH)_2H_2SO_3$ and goes practically to completion with both forms.

	Ne	edles			Plates	3		
	Weight	liglycine hy	drosulfite		Weight	Diglycine i	ıydrosulfite	e
Sample G.	after 6 days	Calc. G.	Found	Sample G.	after 6 days	Calc. G.	Found	
0.1017	0.1538	0.1566	98.22	0.1123	0.1667	0.1729	96.42	
.1127	.1709	.1736	98.45	.0894	.1197	.1377	86.93	

When dry gas and powdered crystals were employed, practically no sulfur dioxide was taken up, the action at best being only very slight, less than one part per hundred in the case of the needle form, and none at all with the plates.

Action of Bromine

Even after 6 days, not enough bromine (an average of 67%) added to the dry powdered crystals to form a monobromo addition product. The needle form, however, was observed to react somewhat more readily than the plates.

Under atmospheric moisture conditions bromine acted upon the two forms as follows.

		Needles		
Sample G.	Wei After 3 days	ght After 6 days	Cale. wt. for glycine monobromide	Calc. wt. for glycine dibromide
0.1166	0.4420		0.2390	0.3653
.1206(b)	.2000	0.2480	.2473	.3780
. 1167	.2044	. 2244	.2394	.3656
		Plates		
.1260	.3800		.2587	.3950
.1066	.3305	.4055	.2187	.3340
.1007	.2947	.3417	.2064	.3160

In this series of experiments, the results are irregular. Sometimes the needle form or the plate form takes up more bromine than the theoretical quantity for a dibromo addition product. In (b) the quantity taken up approximated the monobromo product. According to Falk and Sugiura² the needles form the dibromo and the plates the monobromo product. These investigators state, however, that at times when conditions were apparently suitable for the one form the other was obtained.

When moist bromine was allowed to come in contact with glycine, enough bromine was taken up by both forms in 45 minutes to form about 67% of the monobromo product. After 5 hours, a dark red, liquid mass was obtained. When this was dried, colorless glycine was recovered.

In view of the facts that relatively little bromine adds to glycine in dry form, that varying quantities of moisture change the speed and quantity of bromine addition or absorption, or adsorption, and that the bromine is immediately given off when the compound is allowed to stand in the air, it seems probable that bromine forms no definite chemical compound with either variety of glycine. If all moisture were to be excluded from the apparatus, the glycine and the bromine, it is probable that no bromine would adsorb or add to the glycine at all. Various inorganic salts containing water of crystallization or hydration also add bromine temporarily. Crystallized borax, for instance, adds bromine when exposed under ordinary conditions to bromine vapors in a bell jar. In one experiment 30.2305 g. of borax (weight with container) added 0.0138 g. of bromine in 3 days and 0.0820 g. in 6 days.

Formation of Amino-acetyl Chloride

Attempts were next made to investigate the nature of the compounds formed in Fischer's original experiment with phosphorus pentachloride and acetyl chloride. When 2 g. of glycine was treated with phosphorus pentachloride and acetyl chloride according to Fischer's procedure, the needle form yielded 0.353 g. of the hydrochloride of glycyl chloride, while the plate form yielded 0.345 g., amounting to about 10%. These results indicate that one form might have reverted to the other upon standing after pulverization. The filtrates from the solid residues were distilled under 170 mm. pressure and at from 20–25°. The distillates in both cases contained no nitrogen and consisted chiefly of acetyl chloride. A red oily substance remained in the flasks. When alcohol was added to the oil, that from the needle form warmed but deposited no crystalline substance, while that from the plate form warmed to a greater degree and yielded some crystals of glycine ethyl ester hydrochloride. H. T. Clark' states that acetyl chloride reacts with glycine to form acetyl-glycine.

⁷ Clark, "An Introduction to the Study of Organic Chemistry," Longmans, Green and Co., 1914, p. 290.

The second set of experiments was carried out with 10 g. of the freshly prepared forms without intermission. In these experiments Fischer's results were duplicated, that is, 8.5 g. of the acid chloride was separated from the reaction mixture from needle glycine, corresponding to 49.2% of that calculated for glycyl chloride hydrochloride. The plate form gave a solid residue which when dried weighed 3.0 g., corresponding to 17.3% of the hydrochloride of glycyl chloride. Aniline, water and alcohol all reacted violently and exothermically with the hydrochloride of glycyl chloride from needle glycine.

The 3 g. of substance separated from the reaction mixture from the plate form did not react with aniline or alcohol and dissolved in water without rise in temperature. Its melting temperature was 202°, it contained chlorine and was probably glycine hydrochloride. Analogous to ammonium chloride, its heat of solution was negative. When dissolved in water, treated with silver oxide and hydrogen sulfide, filtered, the filtrate evaporated and the residue crystallized, glycine was obtained. It thus appears that the plate form did not react to form an acid chloride and that the substance that was formed dissolved in the acetyl chloride.

The filtrates were examined as before. They were distilled under reduced pressure at 30°, the residual oil was washed in petroleum ether and was then found to contain phosphorus and chlorine. It was soluble in acetone and ethyl acetate but could not be purified.

In order to study the influence of one constituent at a time, the action of phosphorus trichloride alone on glycine was examined. Even prolonged action or treatment of a suspension of the pulverized needle or plate glycine in phosphorus trichloride yielded no new product, the glycine being recovered unchanged.

Phosphorus pentachloride was next dissolved in carbon disulfide and treated with glycine. No action was observed. Ten g. of each form was mixed with 200 cc. of carbon disulfide and 31.5 g. of phosphorus pentachloride and the mixture stirred for 4 hours. The plate form yielded 11 g. of a white crystalline salt which fumed strongly in the air (due to the presence of hydrogen chloride) even after being washed with carbon disulfide and petroleum ether. After the mass had stood in a vacuum desiccator over phosphorus pentoxide for 12 hours it darkened and became oily and resinous. This action was probably the effect of some phosphorus pentachloride that had not been washed out, as a positive test for phosphorus was obtained. When phosphorus pentachloride and glycine were mixed dry and allowed to stand in a desiccator, an oily mass was formed, similar to that obtained in the experiment with acetyl chloride when phosphorus pentachloride was present.

In the next trial, 10 g. of the plate form of glycine was treated with a larger quantity of carbon disulfide (400 cc.) and much effort was made to

wash out all phosphorus pentachloride with carbon disulfide and petroleum ether. In this manner 7 g. of a white crystalline solid was obtained. This did not fume in moist air, contained only a slight trace of chlorine, melted at 210° and was soluble in carbon disulfide. It was, therefore, not an acid chloride. Upon purification, it proved to be glycine. The needle form under exactly the same conditions yielded 10.4 g. of a white crystalline solid that was soluble in carbon disulfide, insoluble in alcohol and melted at 210°.

From these experiments, we conclude that phosphorus trichloride and phosphorus pentachloride in carbon disulfide solution have no action on either form of glycine. This would indicate that the substance causing the reaction in the Fischer experiment, yielding a chlorine derivative was the acetyl chloride, although the phosphorus pentachloride may have had some influence.

An attempt was made to determine whether any difference existed between the 2 forms of glycine in their action toward esterification reagents; 5 g. of each was boiled under a reflux condenser for 2 days with ethyl iodide and absolute alcohol. There was no evidence of reaction in either case, the glycine separating unchanged after removal of heat. After filtration, the filtrates were extracted with ether and when the ether extract was evaporated only a small quantity of resinous material was obtained. Evaporated with strong hydrochloric acid solution, no crystals were obtained. According to Beilstein, the plate form yields the ethyl ester when treated with absolute alcohol and ethyl iodide in a closed tube.

Summary

- 1. The action of hydrogen chloride, bromine vapor, and sulfur dioxide, with and without moisture, shows that moisture rapidly brings about an equilibrium between the plate and needle forms of glycine, and that any difference to be definitely established must be determined in the absence of water or even atmospheric moisture. The dry crystals do not differ chemically when dried at 103° and pulverized to pass a 0.3 mm.-mesh sieve; neither is there a difference in their moisture content when air-dried and pulverized, or in their decomposition temperatures.
- 2. Bromine did not form a chemical compound with glycine. By varying the quantity of moisture and length of time of contact, varying quantities of bromine can be taken up. The addition, absorption, or adsorption, however, is only temporary.
- 3. It is probable in the Fischer experiment that phosphorus pentachloride does not act directly on glycine to form any acid chloride. From the results obtained with phosphorus trichloride and phosphorus pentachloride, both dissolved in carbon disulfide, it appears that acetyl chloride itself reacted with glycine in the presence of the phosphorus halide to form glycyl

chloride indirectly, together with a number of other substances, some containing phosphorus.

This study of the characteristics of glycine is being continued.

ORONO, MAINE

[CONTRIBUTION FROM THE PHARMACOGNOSY LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

NEW SOURCES OF SANTONIN¹

By Arno Viehoever and Ruth G. Capen Received April 9, 1923

The discovery of a new source of santonin should attract attention, especially because it is now almost impossible to obtain the plant material, wormseed, as well as santonin itself, owing to the unsettled conditions in Russia. Both are now marketed at prices unusually high. Levant wormseed is quoted at \$3.25 to \$3.50 per pound, and santonin at \$172 to \$175 per pound.²

Supplies other than the normal source of santonin, Artemisia cina Bg. (Artemisia maritima var. stechmanniana Bees.), which grows exclusively in the region of Turkestan and Siberia, have been utilized by manufacturers of santonin. It is reported that the plant species Artemisia gallica Willdenow, which is indigenous to France, and Artemisia brevifolia Wallich contain santonin. No definite quantities of santonin are reported in the investigations of Heckel and Schlagdenhauffen³ and, as far as is known, this plant (Artemisia gallica) was never utilized in the manufacture of santonin. Artemisia brevifolia, a form very closely related to Artemisia maritima Linné, growing abundantly in Thibet, has more recently been mentioned as a possible commercial source. In 1921 Greenish and Pearson4 called attention to this source in which they found 0.85% of santonin. Another sample of the same plant, collected at Gurez, yielded 1.09% in the leaves dried at 100°, or 0.76%, calculated upon the air-dry leaves and stems as received.⁵ Whether this material can be utilized as a commercial source is still undecided.

In 19206 a German firm patented a process to isolate santonin from the

- ¹ A preliminary note was presented at the meeting of the American Chemical Society, Birmingham, Ala., April 3–7, 1922. An abstract was published in *Am. J. Pharm.*, 94, 446 (1922).
 - ² Oil, Paint and Drug Reporter, Jan. 10, 1923.
- ³ Heckel, Ed., and Schlagdenhauffen, Fr., "De l'Artemisia gallica Willd., comme plante à santonin, et de sa composition chimique." *Compt. rend.*, 100, 804 (1885).
- ⁴ Greenish, H. C., and Pearson, C. E., "A new source of santonin." *Pharm. J.*, 52, (4th ser.), 243 (1921).
- ⁵ Greenish and Pearson, "Note on the Occurrence of Santonin," *Pharm. J.*, 109, 85 (1922).
 - ⁶ Patentschrift Nr. 346,947, Klasse 120, Gruppe 25, Jan. 11, 1922.

whole herb of Artemisia maritima L., growing in Germany on the North Sea and the Baltic Sea.

Survey of Domestic Species of Santonin

Because of the scarcity of a needed drug, a survey of the domestic forms of Artemisia, as a possible source of santonin, was undertaken by the Bureau of Chemistry. This investigation, not fully completed, has yielded very interesting and promising results.

Procedure

A few of the flower heads of the Artemisia species to be examined were placed in a sublimation apparatus. The apparatus, consisting of a small beaker-like container with a cup extending from the bottom, was immersed in an oil-bath kept at a temperature ranging from 150° to 170°. A cover slip (upon which the sublimate was received) was placed over the opening of the cup. A cooling device and vacuum were also used.

The sublimed santonin was deposited on the cover slip in oily drops, which, upon standing, crystallized in large prismatic plates. By treating the sublimate with ether the formation of santonin crystals was appreciably hastened. Santonin was identified by four tests as follows.

Crystalline Structure.—Santonin forms very characteristic rhombic plates. On account of the solubility of santonin in most solvents having a high index of refraction, only an approximate value for its refractive index, namely, about 1.6, was established.⁸

Melting Point.—Purified santonin melts at 170°. The melting is preceded by a loss of the polarizing power, at 1° or 2° below 170°. The melting point can be readily observed under the microscope when the material is heated in a special heating chamber (micro-melting-point apparatus).

Furfural Reaction.—The sublimate is dissolved in a small quantity of alcohol to which 1 to 2 drops of 2% furfural solution and 1 to 2 cc. of sulfuric acid are added. Upon evaporation of the alcohol the liquid is purplish-red, carmine-red, changing to bluish-violet, and finally shows a black precipitate. Furfural alone with sulfuric acid gives a red.

Formation of Santonin Per-iodide.—This has already been described. ¹⁰ The species examined, the locality from which they were obtained, and the results of the examination are given in Table I.

⁷ This apparatus, as well as a new sublimation flask suitable for this work, is fully described in a paper entitled "Sublimation of Plant and Animal Products, Third Report," by Arno Viehoever, *J. Assoc. Official Agr. Chem.*, 6, 473 (1923).

⁸ Determined by J. F. Clevenger of the Bureau of Chemistry.

⁹ Ref. 7, p. 477.

¹⁰ J. Assoc. Official Agr. Chem., 5, 557-8 (1922).

Table I

Examination of Domestic Artemisia Species

				Furfural test	
Artemisia species	Source	S	ublimate	for santonin	
Atomifera Piper	Washington				
Absinthium L.	North Dakota		Fine crystals ^a		
Albula Wooton	New Mexico				
Annua L.	Arlington Farm,	Va.			
Arborescens Linn.	,		Fine crystals	****	
Aromatica A. Nels.	Idaho		Long needles		
Biennis Willd.	Oregon		Long nectnes		
	New Mexico		Small needles		
Bigelovii A. Gray	California		oman needles	-	
Californica Less.					
Cana Pursh.	New Mexico				
Canadensis Michx.	Wisconsin		Paperson and Paperson		
	Nebraska				
Caudata Michx.	Wisconsin				
	Michigan				
Carruthii A. Wood	New Mexico		Fine crystals		
Dracunculina S. Wats					
Dracunculoides Pursh.			Fine crystals		
Diacancaiolaes I aisii.	Arizona		Many needles	_	
Filifolia Torr.	New Mexico		Fine crystals		
	MEM MEXICO			?	
75 77 77 77	Court D tout		Small needles		
Forwoodii Watson	South Dakota			~	
Forwoodii Watson	North Dakota				
Frauserioides Greene	Colorado		Small needles		
Frigida Willd.	Arlington Farm,	Va.	Fine crystals ^a	• ==	
	New Mexico		Fine crystals	-	
Gallica Willd.			Fine crystals		
Gnaphalodes Nutt.	Arlington Farm,	Va.			
	North Dakota		Annual learning		
Heterophyllea Nutt.	California		Small plates		
Kansana Britton	New Mexico		Fine crystals		
Ludoviciana Nutt.	Arizona		Time crystais	_	
	Utah				
Mexicana Bakeri	New Mexico			- +	
Mexicana Willd.	Mew Mexico		Daines ad		
*****	• • • • •		Prisms ^d	7	
	. :		Oily mass		
	Arizona		- 17		
			Oily mass	Green	to dark blue
			* Repaire wheeled		
Redolens Gray	New Mexico		Fine crystals		
a de a a a granda de la composição de la c	Mexico			· · · · · · · · · · · · · · · · · · ·	
Vulgaris L.	Wisconsin				
	Yosemite Valley			-	
Microcephale Wooton	New Mexico		Fine crystals		
Neo-mexicana Wooton			$Prisms^d$	+	
Pontica L.			Fine crystals	_	
Rhizomatus pubularis	Wyoming			<u> </u>	
Tridentata Nutt.	California		Fine crystals		
Wrightii Rausch.	New Mexico		- Inc crystala		
	TICM TITEVICO		Small needles		
Wrightii Gray		120	oman needles	7	
the second second	*****		Constituents la		
t the engine			Small crystals	*******	
				+	
	· · · · · · · · · · · · · · · · · · ·		Small crystals		
a See en la seconda de la companya	Val 		Oily mass		
			Oily mass	3	
Melting points: a 65°	b 135° 696	0-11	5° d 165°.		

The survey of 56 species of Artemisia showed that santonin can be obtained from Artemisia mexicana Willd., from Artemisia neo-mexicana

Wooton, and probably from Artemisia Wrightii, all of which grow in the region of New Mexico and Mexico.¹¹

Only very small quantities of material were available for experimental work. Attempts to obtain fresh and larger supplies of Artemisia mexicana and Artemisia neo-mexicana have thus far been unsuccessful. Sufficient plants could not be collected in time, and the seeds obtained failed to grow. The closed flower heads, which in the case of Artemisia cina, contain the largest quantities of santonin, were used in the survey whenever possible. In many cases the open flower heads of old plants of various species had to be examined. The negative results, therefore, are not absolute proof of the absence of santonin in the species mentioned.

The results indicate a distinct possibility of utilizing domestic plants, growing as weeds in barren fields, for the manufacture of santonin.

Summary

Of 56 species of domestic Artemisia pronounced tests for santonin were obtained from A. mexicana Willd., from A. neo-mexicana Wooton and probably from A. Wrightii, all of which grew in the region of New Mexico and Mexico.

The results indicate a distinct possibility of utilizing domestic plants, growing as weeds in barren fields, for the manufacture of santonin.

WASHINGTON, D. C.

[Contribution from the Biochemical Laboratory, New York Agricultural Experiment Station]

A STUDY OF THE PHYTOSTEROLS OF CORN OIL, COTTONSEED OIL AND LINSEED OIL¹

By R. J. Anderson with M. G. Moore Received May 7, 1923

Introduction

The present investigation was undertaken in connection with the work on the phytosterols in the fat from corn pollen.² The properties of the phytosterols from corn pollen differed so markedly from other plant phytosterols that we desired to extend the investigation in the hope of finding similar substances in other plant products. But the materials which we examined, corn oil, cotton seed oil and linseed oil, did not yield any phytosterols similar to those found in corn pollen.

The first substance to be investigated was corn oil. The unsaponifiable matter in corn oil was called cholesterol by Hoppe-Seyler,³ but no data were

- 11 Copies of the illustrations of the plants may be obtained from the author.
- ¹ Read at the meeting of the American Chemical Society, New Haven, Conn., April, 1923.
 - ² Anderson, J. Biol. Chem., 55, 611 (1923).
 - * Hoppe-Seyler, "Med. Chem. Unters.," 1866, p. 162.

given regarding the physical or chemical properties of this substance. Hopkins⁴ reported that the "cholesterol" of maize oil melted at 137° to 137.5°, and gave the color reactions of cholesterol. Gill and Tufts⁵ questioned the correctness of the term "cholesterol" as applied to the unsaponifiable matter in maize oil. These authors found that the purified substance melted at 137.5° to 138°, and the acetyl derivative melted at 127.1°, and they concluded that "the above results seem sufficient to prove that the alcohol of maize oil is not cholesterol....the compound studied is undoubtedly identical with the compound found in wheat and rye and described by Burian⁶ under the name of 'Sitosterol'." König and Schluckebier⁷ report the isolation of a phytosterol from corn oil which melted after the seventh recrystallization at 140.4°, and the acetate melted at 137°. The high melting point of this substance must have been due to imperfect or partial acetylation.

Our results agree with those reported by Gill and Tufts. The phytosterol which we isolated from corn oil appeared to be homogeneous. We believe that it is identical with sitosterol and we could not find any evidence of the presence of stigmasterol. Upon bromination of the acetyl derivative by the method of Windaus and Hauth⁸ only a dibromo compound was obtained. Ritter⁹ reported for sitosterol in chloroform solution a specific rotation of —33.91°, while our preparation dissolved in chloroform gave a specific rotation of —34.38°.

Several investigators have reported upon the unsaponifiable matter in cottonseed oil. Bömer and Winter isolated a preparation which melted at 136° to 137°. Siegfeld obtained 3 different crystalline substances from the unsaponifiable matter of cottonseed oil. A phytosterol preparation was finally obtained from the mother liquors which melted at 138.8° to 139.8°, and its acetate melted at 131.5° to 132.5°. König and Schluckebier found a phytosterol which melted at 137° to 138° and the acetate melted at 125.8°, after the fifth recrystallization. Heiduschka and Gloth were unable to find any stigmasterol in the phytosterol from cottonseed oil by the method of Windaus and Hauth. They obtained a dibromo-acetate that melted at 127°, and that upon reduction with zinc

- 4 Hopkins, This Journal, 20, 948 (1898).
- ⁵ Gill and Tufts, ibid., 25, 251 (1903).
- ⁶ Burian, Monatsh., 18, 551 (1897).
- ⁷ König and Schluckebier, Z. Nahr. Genussm., 15, 641 (1908).
- ⁸ Windaus and Hauth, Ber., 39, 4378 (1906).
- ⁹ Ritter, Z. physiol. Chem., 34, 461 (1901).
- ¹⁰ For a more complete list of references see Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," MacMillan and Co., Ltd., London, 6th Ed., 1922, vol. I, p. 280 and vol. II, pp. 208–209.
 - 11 Bömer and Winter, Z. Nahr. Genussm., 4, 865 (1901).
 - 12 Siegfeld, ibid., 7, 577 (1904).
 - 13 Heiduschka and Gloth, Pharm. Zentr., 49, 863 (1908).

dust and saponification gave the original phytosterol which melted at 136°. In an investigation of the "Soapstock" residues from cottonseed oil, Wagner and Clement¹⁴ isolated a phytosterol which after 3 or 4 recrystallizations melted at 137.5° to 138°. The above-mentioned authors were unable to separate any stigmasterol from the preparation by the method of Windaus and Hauth,⁸ thus confirming the results of Heiduschka and Gloth.¹³ They were able, however, by repeated recrystallization to separate this phytosterol into 2 fractions. One melted at 139°, and gave an acetate melting at 125°; the other melted at 130–131°, and its acetate melted at 120°. Although both of these fractions gave the usual phytosterol reactions, these authors believed that the phytosterol of cottonseed oil was not homogeneous, but consisted of two different substances.

Matthes and Heintz¹⁵ separated the unsaponifiable matter obtained from cottonseed oil into a solid and a liquid portion. The liquid portion was further separated by distillation under reduced pressure into several fractions from which, however, no definite compounds could be obtained.

The solid portion consisted of phytosterol which melted at 139°. Its optical rotation was —23.14° which is much lower than has usually been reported for phytosterol. The acetyl derivative gave only a dibromo derivative melting at 125°, which upon reduction with zinc dust gave the original phytosterol melting at 139°.

Our results confirm the findings of Wagner and Clement. By fractional crystallization we were able to separate the phytosterol of cottonseed oil into 2 fractions that differed slightly in their melting points and also in optical rotation.

The phytosterol of linseed oil was investigated by Bömer and Winter¹¹ who isolated a preparation which melted at 137° to 138°, and the acetate melted at 128° to 129°.

We were able to separate the phytosterol of linseed oil by fractional crystallization into 2 fractions that were very similar to those we obtained from cottonseed oil. We believe, therefore, that cottonseed oil and linseed oil contain at least 2 phytosterols that differ in their melting points and also in their optical rotation. These substances, however, so far as one can determine by chemical analysis, are identical in composition and they give identical color reactions. The differences in physical properties which we have noted must depend upon slight variations in constitution.

It is very evident that the phytosterol occurring in plants is not a single homogeneous substance but may consist of 2 or more fractions that differ slightly in physical properties and sometimes in chemical composition, particularly stigmasterol. Occasionally these fractions may be separated with ease and in great purity as shown by Windaus and Hauth.⁸ However,

¹⁴ Wagner and Clement, Z. Nahr. Genussm., 17, 266 (1909).

¹⁵ Matthes and Heintz, Arch. Pharm., 247, 161 (1909).

in some mixtures of phytosterols this method is not applicable as shown by Wagner and Clement¹⁴ in the case of the phytosterols from cottonseed oil.

Phytosterols occur in all parts of the plants¹⁶ but the function of these substances in the metabolism of the plant is not known. The fact that phytosterols are largely deposited with the fats in seeds and pollen grains would seem to justify the assumption that these substances play an important role in the life of the plant cells.

An important relation must undoubtedly exist between the phytosterols and the corresponding alcohol which occurs in animal cells and tissues, namely cholesterol, the phytosterols contained in vegetable foods being the source of the cholesterol found in animal tissues.

Experimental Part

Crude corn oil¹⁷ was saponified in lots of 300 g. by boiling it with 600 cc. of alcoholic potassium hydroxide. Two kg. of the oil was saponified in this way. The soap solution was largely diluted with water and extracted with 3 portions of ether. The ethereal solution was washed with dilute potassium hydroxide and with water, filtered and evaporated. The residue was yellowish-brown in color and it contained some oily substance. It was again boiled with 300 cc. of alcoholic potassium hydroxide for ¹/₂ hour. As the solution cooled, the greater part of the substance crystallized. This was filtered off, washed in dil. alcohol until free from alkali, and dried in a vacuum over sulfuric acid.

A smaller amount of material was recovered from the filtrate after diluting it with water and extracting with ether. After the ether had evaporated an oily residue remained that was dissolved in hot alcohol. A mixture of crystals and a yellow oil separated as the solution cooled. The oil was eliminated by repeated crystallization from alcohol, and we obtained finally a pure snow-white product that crystallized in plates. The dry substance melted 18 at 137.5°.

The first crystalline product mentioned above weighed 16.8 g. It was recrystallized thrice from 300 cc. of 95% alcohol and was then snow-white in color. It crystallized in 2 forms, either as compact elongated plates when the solution was cooled slowly, or in very large thin plates when the solution was cooled rapidly. The purified substance weighed 12.6 g. Heated in a capillary tube it melted at 137.5°. Drying in a vacuum at 105° did not change its melting point. It gave the Liebermann-Burchard reaction and it readily absorbed bromine in chloroform solution. For analysis it was dried at 105°, in a high vacuum over phosphorus pentoxide.

Analyses. Subs., 0.1434: H_2O , 0.1578; CO_2 , 0.4437. Calc. for $C_{27}H_{45}OH$ (386): C, 83.93; H, 11.91. Found: C, 84.38; H, 12.31.

¹⁶ Czapek, "Biochemie der Pflanzen," Gustav Fischer, Jena, 2nd ed., 1905, vol. I, p. 163.

¹⁷ The crude and refined corn oils used in this investigation were kindly furnished by Mr. Lloyd Bosworth of the Patent Cereals Company, Geneva, N. Y.

¹⁸ Unless otherwise specified, the melting points given in this paper are uncorrected.

The substance was again recrystallized four times from absolute alcohol and analyzed after it was dried as described above.

Analysis. Found: C, 83.72; H, 12.41.

The substance again melted at 137.5° . It was then recrystallized from 80% alcohol. The melting point did not change. After it had been dried as described above it was analyzed.

Analysis. Found: C, 83.78; H, 12.12.

In chloroform solution its specific rotation was $[\alpha]_{\rm D}^{20} = -34.38^{\circ}$.

The analyses agree closely with the calculated composition of phytosterol, $C_{27}H_{45}\mathrm{OH}$, and the melting point is identical with that of sitosterol.

Water of Crystallization.—The various preparations that we analyzed contained some water of crystallization.

Analyses. Subs., 0.1532, 0.1384, 0.1093: loss on drying at 105° , 0.0063, 0.0054, 0.0036. Cale. for $C_{27}H_{45}OH + H_2O$: H_2O , 4.45. Found: 4.11, 3.90, 3.29.

The first sample had been crystallized from 95% alcohol and dried in a vacuum over sulfuric acid. The second had been crystallized from absolute alcohol and dried in the air. The third had been crystallized from 80% alcohol and dried in the air.

It is evident from the above data that all of our preparations contained less water of crystallization than is required for $1~\rm{H}_2O$.

Acetyl Derivative.—The acetyl derivative was prepared by boiling 1 g. of phytosterol with 35 cc. of acetic anhydride. The acetic anhydride was distilled in a vacuum and the residue purified by recrystallizations from absolute alcohol. The substance was obtained as snow-white crystals that melted at 127°. It did not lose in weight on drying in a vacuum over phosphorus pentoxide.

Analysis. Subs., 0.1410: H_2O , 0.1435; CO_2 , 0.4207. Calc. for $C_{27}H_{45}O$.OC.CH₃ (428): C, 81.31; H, 11.21. Found: C, 81.37; H, 11.38.

Bromination of Phytosterol.—The direct bromination of phytosterol did not lead to a satisfactory product. To a solution of 1 g. of dry phytosterol in 10 cc. of ether was added 0.85 g. of bromine dissolved in 10 cc. of glacial acetic acid. Nothing crystallized from this solution even after it had stood in a freezing mixture for some time. The substance was therefore extracted with ether, the ethereal solution was washed with dil. alkali and water, filtered and the ether evaporated. The yellowish crusts that remained weighed 1.4 g. after they had dried in a vacuum over sulfuric acid. This indicates that 2 atoms of bromine had been absorbed. The substance could not be obtained in crystal-line form from any of the usual solvents. It separated more readily from methyl alcohol than from any other solvent but the product was amorphous.

The bromination of the acetyl derivative was more successful. A solution of 5.1 g. of the acetyl derivative in 30 cc. of ether was brominated by the method of Windaus and Hauth.⁸ After it had stood for about ¹/₂ hour at room temperature a small amount of substance without any distinct crystal form separated from the bromination mixture. When the flask was placed in a freezing mixture the amount of this substance was greatly increased. It was filtered, washed thoroughly in cold glacial acetic acid and dried in a vacuum over sulfuric acid and potassium hydroxide. The dry substance showed only a faint yellowish color, and it weighed 3.3 g.

The remainder of the bromine derivative was obtained when the filtrate from the precipitate described above was diluted with water after the ether had been distilled under reduced pressure. It separated as a voluminous, amorphous precipitate. This was filtered off, washed with water and dried in a vacuum over sulfuric acid. The dry substance was brownish and weighed 3.7 g.

The total weight of the bromine derivatives was 7 g., which represents a quantitative yield provided 2 atoms of bromine had been absorbed.

These fractions were purified separately. The first fraction separated from absolute alcohol in the form of microscopic granules that showed no definite crystalline structure. The product was snow-white. It was impossible to obtain the substance in definite crystals from any of the usual solvents. When heated in a capillary tube the substance melted at 120° to 120.5°. It did not give the Liebermann-Burchard reaction. Evidently the development of the color in this reaction depends upon the double bond.

It did not lose in weight on drying at 105° in a high vacuum over phosphorus pentoxide.

Analyses. Subs., 0.2075: H_2O , 0.1569; CO_2 , 0.4500. Subs., 0.1780: AgBr, 0.1182. Calc. for $C_{27}H_{46}O$.CO.CH₂Br₂ (587.84): C, 59.20; H, 8.16; Br, 27.19. Found: C, 59.14; H, 8.46; Br, 28.25.

The bromine found was about 1% too high but it is evident that the substance was essentially a dibromo-phytosterol acetate.

The second preparation was purified in the same way and gave an identical product that melted at 120° to 120.5° .

It is evident from the above results that the phytosterol of corn oil does not contain any stigmasterol.

Regeneration of Phytosterol from the Bromo-acetyl Derivative.—To 3 g. of the bromo-acetyl derivative dissolved in 200 cc. of alcohol was added 10 cc. of glacial acetic acid and the solution was boiled for 3 hours with 15 g. of zinc dust under a reflux condenser. More zinc dust was added in small portions from time to time. The excess of zinc was then filtered off and the filtrate boiled with 40 g. of potassium hydroxide for 1 hour. The phytosterol was extracted with ether and purified by recrystallization several times from absolute alcohol. So far as one could judge by crystal form, solubilities and reactions, the substance was identical with the original phytosterol and melted at 137.5°.

Quantitative Determination of the Unsaponifiable Matter in Corn Oil.—We followed the method outlined by Bömer¹⁹ in determining the unsaponifiable matter in corn oil. It was found necessary, however, to extract the soap solution 7 times with ether before all of the crystallizable phytosterol had been removed. On evaporation of the ether after the sixth extraction there was a slight but distinct crystalline residue. Even the seventh extraction left a slight residue on evaporation of the ether but this was a yellow oily substance that did not show any crystals of phytosterol.

The total residue after the evaporation of the ether was again boiled with alcoholic potassium hydroxide, diluted with water, and extracted thrice with ether. After the ethereal solution had been washed and filtered, it was evaporated and the residue dried to constant weight at 100° and weighed.

The crude phytosterol thus obtained was mixed with some yellow oil and the residues from the crude corn oil contained a larger amount of this oily substance than those from the refined oil. We did not determine the nature of this unsaponifiable oily substance but it would seem worthy of further investigation.

¹⁹ Börner, Z. Nahr. Genussm., 1, 21 (1898).

In each determination 50 g. of oil was saponified and the following results were obtained.

Cruc	Crude corn oil Unsaponifiable		Refined edible corn oil Unsaponifiable			
	G.	%	G.	%		
1	.0740	2.15	0.8346	1.67		
1	.0018	2.00	.8260	1.65		
. 0	.9711	1.94	.8654	1.73		
0	.9813	1.96				
, -		#	***************************************			
Av. 1	.0070	2.01	Av. 0.8420	1.68		

It is evident from the above figures that corn oil contains a high percentage of unsaponifiable matter and that in the process of refining less than 0.5% of the unsaponifiable material is removed.

The Phytosterol of Cottonseed Oil

About 2 kg. of cottonseed oil²⁰ was saponified and the phytosterol isolated as described under corn oil.

The unsaponifiable residue left on evaporation of the ether was dark brown, largely due to the admixture of a dark oil. The substance was dissolved in 500 cc. of methyl alcohol and the solution boiled with norite, filtered and allowed to cool. It was still dark in color and the product that separated in large thin plates was yellowish-brown. It was recrystallized thrice from methyl alcohol and 4 times from ethyl alcohol. The dry substance weighed 2 g. and was slightly yellowish; m. p., 135°. The mother liquors were saved and examined, as will be described later.

Acetyl Derivative.—For further purification the phytosterol was acetylated and the acetyl derivative recrystallized twice from methyl alcohol, from which it crystallized in rosets of fine needles, and twice from ethyl alcohol from which it crystallized in thin plates. After the final filtration, washing the substance in cold alcohol and drying it in a vacuum over sulfuric acid, it weighed 1.7 g. It was snow-white; m. p., 119°. It did not lose in weight on drying at 105°, in a high vacuum over phosphorus pentoxide.

Analyses. Subs., 0.1103: H_2O , 0.1151; CO_2 , 0.3288. Calc. for $C_{27}H_{45}O$.CO.CH₃ (428): C, 81.31; H, 11.21. Found: C, 81.30; H, 11.67.

Saponification of Acetyl Derivative.—The remainder of the purified acetyl derivative was saponified with alcoholic potassium hydroxide and the phytosterol extracted with ether in the usual way. It was crystallized from methyl alcohol and recrystallized from ethyl alcohol from which it separated in thin colorless plates. The dry product was snow-white and it weighed 1.1 g. Heated in a capillary tube it melted at 134-135°. Drying it at 105° in a vacuum over phosphorus pentoxide did not change the melting point. The substance was again recrystallized from 95% ethyl alcohol, but the melting point was still 134° to 135°.

Water of Crystallization.—The purified phytosterol suffered some loss in weight when dried at 105° in a vacuum over phosphorus pentoxide, corresponding to about 0.5 H₂O.

Analyses. Subs., 0.1201, 0.8760: loss, 0.0033, 0.0185. Calc. for $C_{27}H_{48}OH.H_2O$: H_2O , 4.45. Calc. for $C_{27}H_{45}OH.^1/_2H_2O$; H_2O , 2.27. Found: 2.74, 2.11; av., 2.42.

²⁰ The oil was bought in the open market in sealed tin cans which were marked "Wesson Oil. The Southern Cotton Oil Company."

The purified and dried phytosterol in chloroform solution gave $[\alpha]_{\rm p}^{20}$, —33.61°. After drying in a vacuum at 105°, over phosphorus pentoxide the substance was analyzed.

Analysis. Subs., 0.1168: H_2O , 0.1277; CO_2 , 0.3588. Calc. for $C_{27}H_{45}OH$: C, 83.93; H, 11.91. Found: C, 83.78; H, 12.23.

Phytosterol from the Mother Liquors.—The total mother liquors from which the phytosterol preparation described above had been crystallized, were evaporated in a vacuum. The residue was crystallized several times from methyl alcohol until it was snow-white. It was then acetylated and the acetyl derivative purified by recrystallization from ethyl alcohol. It was saponified by alcoholic potassium hydroxide, extracted with ether, and the product was recrystallized many times from methyl alcohol. It was snow-white and crystallized in large thin plates. After drying in the air it weighed about 1 g.; m. p., $138-139^{\circ}$. After the substance was again recrystallized from methyl alcohol the melting point was still the same; in chloroform $[\alpha]_{D}^{20}$, -34.19° .

When dried at 105° in a vacuum over phosphorus pentoxide the substance was found to contain about the same amount of water of crystallization as the first preparation.

Analyses. Subs., 0.1192, 0.7807: loss, 0.0036, 0.0212. Found: H_2O , 3.02, 2.71; av., 2.86.

The dried preparation was analyzed.

Analysis. Subs., 0.1156: H₂O, 0.1257; CO₂, 0.3546. Calc. for C₂₇H₄₅OH (386): C, 83.93; H, 11.91. Found: C, 83.65; H, 12.16.

Acetyl Derivative.—The acetyl derivative prepared from this fraction and recrystallized from methyl alcohol melted at 124°. It was recrystallized several times without change in the melting point.

The 2 phytosterol preparations described above gave identical colors in the Liebermann-Burchard reaction and both preparations absorbed bromine in chloroform solution.

It is evident from the data obtained that the phytosterol contained in cottonseed oil is not homogeneous but consists of at least 2 fractions which differ in melting point and probably in optical rotation since the rotation was slightly greater in the fraction having the higher melting point. If there are 2 phytosterols in cottonseed oil they have apparently the same chemical composition. The differences in physical properties must depend upon slight differences in constitution. It seems doubtful whether these products can ever be separated into homogeneous substances by simple recrystallization.

The Phytosterol of Linseed Oil

The crude phytosterol was isolated from 2 kg. of saponified raw linseed oil in the manner described under corn oil.

The residue obtained on the final evaporation of the ether contained a considerable amount of dark brown oil. This oil was eliminated by recrystallizing the substance several times from ethyl alcohol and then from methyl alcohol but the crystals retained a brownish color. The alcoholic solution was finally decolorized with norite and the phytosterol was obtained pure white in color. The substance was now recrystallized 5 times from methyl alcohol from which it separated in colorless plates. The dry product was snow-white and it weighed 2.8 g. Heated in a capillary tube it began to soften at 132° and to melt at 134°, but it was not completely fluid until heated to 136°. The mother liquors were examined, as will be described later.

Acetyl Derivative.—The whole substance was acetylated and the product crystallized from acetic anhydride. It was then twice recrystallized from 95% alcohol from which it separated in small plate-shaped crystals. It was snow-white and weighed 2.4 g. It softened at 122° and melted at 124°. It did not lose in weight when dried at 105° over phosphorus pentoxide.

Analysis. Subs., 0.1246: H_2O , 0.1299; CO_2 , 0.3709. Calc. for $C_{27}H_{48}O$.CO.CH₃ (428): C, 81.31; H, 11.21. Found: C, 81.18; H, 11.66.

Saponification of Acetyl Derivative.—The balance of the acetyl derivative was saponified with alcoholic potassium hydroxide and the phytosterol was isolated in the usual way. After it had been recrystallized several times from alcohol it was obtained as snow-white, plate-shaped crystals which weighed 1.9 g. It began to soften at 130° but it was not melted to a clear fluid until heated to 134°. When dried at 105° in a high vacuum over phosphorus pentoxide it lost 2.37% in weight, corresponding to 1/2 mol. of water; in chloroform solution $[\alpha]_{D}^{20}$, —31.16°. The dry substance was analyzed.

Analysis. Calc. for C₂₇H₄₅OH(386): C, 83.93; H, 11.91. Found: C, 83.88; H, 12.34.

Phytosterol from the Mother Liquors.—The mother liquors left on crystallizing the above preparations were saved, concentrated in vacuum and the material that crystallized as the solution cooled was purified by recrystallization from methyl alcohol until it was snow-white. This fraction weighed 1.4 g.; m. p., 138°; in chloroform solution, $[\alpha]_{D}^{20}$, —34.22°.

Water of Crystallization.—The loss in weight when the substance was dried at 105° in a high vacuum over phosphorus pentoxide corresponded to $^{1}/_{2}$ H₂O.

Analyses. Subs., 0.1045, 1.0131: loss, 0.0028, 0.0186. Calc. for $C_{27}H_{45}OH^{1/2}H_{2}O$: $H_{2}O$, 2.27. Found: 2.67, 1.83; av., 2.25.

The dried preparation was analyzed.

Analysis. Subs., 0.1017: H_2O , 0.1125; CO_2 , 0.3130. Calc. for $C_{27}H_{48}OH$ (386): C, 83.93; H, 11.91. Found: C, 83.93; H, 12.37.

Acetyl Derivative.—The acetyl derivative was prepared in the usual way and allowed to crystallize from acetic anhydride. It was recrystallized from methyl alcohol from which it separated in tufts of needles. The product was snow-white; m. p., 129-130°. Both fractions gave identical colors with the Liebermann-Burchard reaction.

The data obtained indicate that the phytosterol contained in raw linseed oil is very similar to the phytosterol of cottonseed oil. From both oils 2 fractions of phytosterol were isolated one of which melted at 134°, and the other at 138°. The higher-melting fraction showed a slightly higher specific rotation. However, the acetyl derivatives of the phytosterol from linseed oil melted 5° higher than the corresponding products derived from cottonseed oil.

It is an interesting point that the higher-melting fractions of phytosterol were always obtained from the mother liquors.

Summary

- 1. Corn oil contains a relatively high percentage of unsaponifiable matter, amounting in the crude oil to 2.01% and in the refined edible oil to 1.68%. This unsaponifiable matter consists largely of phytosterol which is identical with sitosterol. Its melting point was 137.5° , and the optical rotation of the dry phytosterol was -34.38° . The acetate melted at 127° . The phytosterol of corn oil does not contain any stigmasterol.
- 2. Cottonseed oil contains at least two phytosterols which differ in melting points and probably in optical rotation. Two fractions of phytosterol were separated by fractional crystallization: (a) m. p., 138-139°;

 $[\alpha]_D^{20}$, —34.19°; the acetate melted at 124°; (b) m. p., 134-135°; $[\alpha]_D^{20}$, —33.61°; the acetate melted at 119°.

The complete separation of these fractions by crystallization is very difficult, if not impossible, and we do not believe that either of the above preparations was homogeneous.

3. Linseed oil contains at least two phytosterols which differ in melting point and optical rotation. As in the case of cotton seed oil 2 fractions of phytosterol were separated by fractional crystallization: (a) m. p., 138° ; $[\alpha]_D^{20}, -34.22^{\circ}$; the acetate melted at $129-130^{\circ}$; (b) m. p., not sharp, 134° ; $[\alpha]_D^{20}, -31.16^{\circ}$; the acetate melted at 124° .

None of the phytosterol preparations that we isolated contained 1 molecule of water of crystallization. The loss in weight on drying was somewhat irregular but corresponded more nearly to 1/2 molecule of water of crystallization.

Mixtures of phytosterols such as are obtained from cottonseed oil and linseed oil are so nearly alike in solubility in the usual solvents that it is practically impossible to effect a complete separation by simple fractional crystallization.

GENEVA.	

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A QUANTITATIVE METHOD FOR THE DETERMINATION OF TOTAL SULFUR IN BIOLOGICAL MATERIAL¹

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The estimation of total sulfur in biological materials has been the subject of many investigations. The most generally recognized source of error, the difficulty of forming a pure barium sulfate, has been largely eliminated by the now well-known modifications introduced as a result of the careful studies by Folin,² Allen and Johnston,³ Johnston and Adams⁴ and Krieble and Mangum.⁵ There are, however, several other factors which have not been sufficiently emphasized. These are complete retention of the sulfur, complete oxidation to sulfate and complete precipitation of sulfate in blanks and in materials low in sulfur. The first two factors appear to be well controlled in the special methods for total sulfur in urine as developed by

- ¹ The greater part of the experimental work of this paper was carried out by Miss Mabel Stockholm in 1918 as part of the requirement for the degree of Master of Science.
 - ² Folin, J. Biol. Chem., 1, 130 (1905).
 - ³ Allen and Johnston, This Journal, 32, 588 (1910).
 - 4 Johnston and Adams, ibid., 33, 829 (1911).
 - ⁵ Krieble and Mangum, ibid., 41, 1317 (1919).

Folin,² Benedict,⁶ Denis⁷ and Modrakowski.⁸ Urine, however, is a very special case in which by far the greater part of the sulfur is already in the sulfate form and, in which we are dealing with relatively large amounts of sulfur as compared with the amount of organic matter to be oxidized. It is a very different matter when it is necessary to oxidize several g. of dry tissue in order to obtain a weighable amount of barium sulfate. This at once introduces the three difficulties referred to.

The incomplete retention of the total sulfur, due either to a loss by volatilization or to incomplete oxidation or both appears to be the most logical source of error in the usual fusion methods with dry sodium carbonate and potassium nitrate or dry sodium peroxide. The same is true for the wet, acid combustion methods. These predictions have been confirmed in this study and in part by earlier studies. Not until after the completion of this work did the authors come across the excellent and almost completely ignored work of Barlow9 who showed the loss of sulfur in the usual dry fusion and wet, acid combustion methods to be due to volatilization. The method which Barlow finally developed is no doubt a reliable one, but it is too cumbersome for general biological application. In view of the impossibility of retaining all sulfur in the usual methods here considered the only alternative is one of two procedures. It is either a complete oxidation of the material by fusion in the presence of an excess of base in a closed vessel or the oxidation of the sulfur in an aqueous alkaline solution to a less volatile form, with the subsequent oxidation of the organic matter by fusion or by a wet, acid oxidizing method. The former involves the use of a specially devised Parr bomb as now employed by the Association of Agricultural Chemists. 10 By the use of this modification investigators working on sulfur problems in plants have found that seeds and plants contain much more sulfur than had previously been reported. This method is not likely to be generally adopted on account of the necessity of the special bomb.

The difficulties of the second alternative, that of wet oxidation in an alkaline solution, we overcame by the use of hydrogen peroxide in concentrated form. Here, also, we later found numerous confirmations as to the value of this reagent for oxidizing reduced sulfur. Thus, as early as 1884 Classen and Bauer¹¹ used hydrogen peroxide for the complete oxidation of sulfides and sulfites. This was confirmed by many other studies and especially by Klemmer¹² and Petersen.¹³ The former uses it for the

- ⁶ Benedict, J. Biol. Chem., 6, 363 (1909).
- ⁷ Denis, ibid., **8**, 401 (1910).
- ⁸ Modrakowski, Z. physiol. Chem., 38, 562 (1903).
- 9 Barlow, This Journal, 34, 342 (1904).
- 10 Latshaw, J. Assoc. Official Agr. Chem., 5, 136 (1921).
- 11 Classen and Bauer, Ber., 16, 1061 (1884).
- 12 Klemmer, Chem.-Ztg., 46, 79 (1922).
- 13 Petersen, Z. anal. Chem., 42, 406 (1903).

complete oxidation of sulfur in gas and Petersen reports the quantitative oxidation of sulfur in the forms of sulfides, thio-urea, thiocarbanilide and of carbon disulfide by hydrogen peroxide in alkaline solutions. Folin.2 in fact, uses essentially the same principle in evaporating the urine after the addition of several g. of sodium peroxide and subsequently oxidizes other constituents by fusion with the addition of more sodium peroxide. As stated before, this method is reliable for urine, but the subsequent peroxide fusions are not applicable to tissues in general unless conducted in a homb. Unless this precaution is taken the chances are that the analyst will lose many estimations due to the explosive combustion, especially when the material contains considerable carbohydrate. We therefore devised our method so as to follow the oxidation by hydrogen peroxide by a second process of acid oxidation with nitric acid and bromine. The results are very satisfactory, as indicated in the table, and as found by experience in the use of the method in other studies. The presence of nitrate in sulfate precipitations has been severely criticized, but the very high results reported as due to the presence of nitrates have been obtained under conditions where the precipitations were carried out in small volumes with relatively high concentrations of nitrates. Under the conditions employed here, that is, of precipitating from a volume of 500 to 600 cc. and digesting on the steam-bath for 10 to 12 hours before filtering and washing, the error is a very slight one. In fact the slight difference of 0.5 to 1.0 mg. of barium sulfate in a total of 0.1125 g. may easily be due to a trace of sulfate in the relatively large amounts of reagents employed. Furthermore, this is corrected by the introduction of a true blank estimation as practiced in this Laboratory for the last 8 or 10 years.

The basis of this true blank test is as follows. It is a very common experience to find no sulfate precipitated in the usual length of time in blank estimations and in other cases where it is known that small amounts of sulfur must be present. If the solution is permitted to stand several days these traces of sulfate may be precipitated. This is especially true when such small amounts of sulfate are to be precipitated from a 500 to 600cc. volume containing 25 to 30 g. of soluble salts. When, however, a known amount of sulfuric acid is added to such solutions, the usual rapid and complete precipitation of barium sulfate is observed. In view of the very satisfactory results obtained in this and other laboratories by the use of this procedure, we have adopted the plan of consistently adding 10 cc. of 0.1 N sulfuric acid to every sulfur estimation including the blank tests. The value obtained in the blank tests is, of course, subtracted from the unknowns and the differences give values truly corrected for blank sulfur in the reagents and procedure.

Experimental Part

In view of the nitric acid oxidation methods suggested by Wolf and Oster-

berg, ¹⁴ by Konschegg¹⁵ and by Halverson, ¹⁶ we tried various modifications of these acid oxidation methods on pure cystine and in no case could we obtain theoretical values. In all estimations careful blank tests were made. Oxidation by bromine in alkaline solution with subsequent oxidation by nitric acid gave the highest results, that is 22.26 to 25.06% of sulfur as compared with the calculated value of 26.69%.

A few preliminary trials in which we attempted first to oxidize cystine in an alkaline solution by means of hydrogen peroxide and later complete the oxidation by nitric acid indicated possibilities by this method of oxidation. After a number of attempts with various modifications we finally devised the new Perhydrol-nitric acid method by means of which we obtained theoretical values for cystine after the proper correction for carefully run blank estimations. The method thus developed was then applied in parallel with the ordinary sodium carbonate-potassium nitrate fusion method to various types of biological material containing different forms of organically combined sulfur. The ordinary fusion method and the new Perhydrol-nitric acid method as used in these studies are given in detail below, and the results obtained after proper corrections for blanks are given in Table I.

Fusion Method

Reagents.—The fusion mixture was prepared by thoroughly grinding and mixing 225 g. of potassium nitrate with 750 g. of anhydrous sodium carbonate. 0.1 N Sulfuric acid and 10% barium chloride solution were used.

Procedure.—A sample of 0.5 to 2.0 g. is thoroughly mixed with 15 g. of the fusion mixture in a 50×70 mm. nickel crucible. Over this mixture is placed a cover of 10 g. of fusion mixture. The crucible is covered and heated very gradually over an alcohol lamp. If smoke escapes from the crucible the flame is lowered and the heating is continued and gradually increased until, with the flame almost touching the crucible, very little or no smoke is developed after heat has been applied for an additional hour at that temperature. When thus thoroughly charred, without loss due to visible "smoking," the contents of the crucible are thoroughly mixed, the crucible is covered and then heated for 10 minutes in a medium sized flame on a Roger's burner.

After the fusion mass has cooled, it is dissolved in about 400 cc. of water in a flask and 40 cc. of coned. hydrochloric acid is added. This is boiled in a flask to remove the carbon dioxide and then evaporated to dryness in a disk on the steam-bath. When completely dry, the mass is moistened with 20–25 cc. of coned. hydrochloric acid and again evaporated to dryness. This same treatment is repeated once more.

The mass of salts is next dissolved in 300 to 400 cc. of distilled water,

¹⁴ Wolf and Osterberg, Biochem. Z., 29, 429 (1910).

¹⁵ Konschegg, Arch. ges. Physiol. (Pflüger's), 123, 274 (1908).

¹⁶ Halverson, This Journal, 41, 1494 (1919).

10 cc. of concd. hydrochloric acid added, and the whole transferred to a 500cc. volumetric flask and accurately made up to 510 cc. The well-mixed solution is then filtered through a dry filter into a dry 500cc. volumetric flask and, after exactly 500 cc. has been collected, it is transferred to a liter beaker together with 100-200 cc. of rinsing water. To this is now added 10 cc. of 0.1 N sulfuric acid solution and after the mixture has been heated to boiling, the 10 cc. of a 10% barium chloride solution is added, drop by drop. The boiling is continued for 10 to 15 minutes and then the mixture is heated for 10 to 12 hours before it is filtered and washed as usual. The filter paper and precipitate are cautiously burned and weighed. Blank estimations are made in exactly the same way. After the value found in the blank has been subtracted from the total weight the difference represents, of course, only 500/510 of the original sample.

Perhydrol-Nitric Acid Method

- (1) Reagents.—(a) A 25% solution of sodium hydroxide by volume; (b) Perhydrol or Superoxol, a 30% solution of hydrogen peroxide; (c) furning nitric acid; (d) bromine; (e) 0.1 N sulfuric acid; (f) a 10% solution of barium chloride.
- (2) Procedure.—Into a 100cc, nickel crucible (50×70 mm.) containing 10 cc. of the 25% sodium hydroxide solution is transferred 0.5 to 2.0 g. of the substance. The covered crucible is then heated on the steam-bath until the mass is almost dry. This requires several hours, but causes considerable decomposition of the complex substances present, so that the sulfur in particular can later be easily oxidized. In case the evaporation has proceeded too rapidly it is best to add again about 10 cc. of water and to repeat the slow evaporation. To the slightly moist material 5 cc. of Perhydrol is added very gradually. In some cases it is necessary to stir the mass with a glass rod or to add a few drops of water so as to distribute the reagent properly. During this treatment the heating is continued on the steam-bath.

The material thus partially oxidized is next transferred to a 300cc. Kjeldahl flask, acidified with nitric acid and concentrated over a free flame until salts begin to separate. This concentrated solution is then oxidized, while boiling, by the gradual addition of fuming nitric acid and bromine until 10 cc. of acid and 40 to 50 drops of bromine have been used. With material low in, or free from, fat this treatment is usually sufficient to bring about complete oxidation of the organic matter. The solution is next evaporated almost to dryness and after water has again been added evaporation is repeated to remove most of the nitric acid. When the water solution of this material is not absolutely clear it is filtered and after it has been neutralized with sodium hydroxide and diluted to about 600 cc. it is acidified by the addition of 10 cc. of concd. hydrochloric acid. The 10 cc. of 0.1 N sulfuric acid is added and the precipitation and estimation are con-

ducted as usual and as described for the fusion method. Blank estimations must be made in exactly the same way with the same amounts of reagents.

In case considerable lipin material is present, such as in nerve tissue, egg yolk, etc., drops of lipin or fatty acid remain unoxidized by the above procedure. These, we find, can be filtered off after the mass has cooled without any loss of sulfur, but we consider it safer to modify the method so as to make the oxidation more efficient and prolonged. By conducting the oxidation by nitric acid and bromine in a flask provided with a glass-stoppered reflux condenser and continuing the boiling for 24 hours on an electric plate we were able to decompose completely egg yolk and a sulfo-lipin preparation from brain tissue.

TABLE I

	ANALYTIC	AL KESUI	LTS			
Substance analyzed	Fusion i Substance taken G.	nethod Corrected BaSO4 ^a G.	i S %	Perhydro Substance taken G.	ol method Corrected BaSO4 ^a G.	s %
Pure cystine (calc. 26.69% of S)	0.1416	0.2555	25.27	0.1541	0.2998	26.62
en e	.1494	.2627	24.56	.1120	.2171	26.61
Fat-free dried tissue No. 6	8496	.0546	0.882	1.3718	.0916	0.909
	1.7334	.0998	.853	1.2004	.0780	.895
Fat-free dried tissue No. 4	1.7289	.1025	.814	1.2119	.0722	.816
	1.8028	.1033	.782	1.3459	.0783	.812
Fat-free dried tissue No. 7	1.7446	.0438	.345	1.5591	.0563	.496
	1.7180	.0465	.366	1.4235	.0520	.498
Fat-free dried tissue No. 1	1.4679	.0537	.507	1.5672	.0615	.538
	1.3614	.0491	.492	1.5690	.0605	. 529
Sulfo-lipin from brain tissue	1.3590	.0569	.575	1.3694	.0587	. 581
	1.5446	.0614	.545	1.3989	.0591	.581
Air-dried egg yolk	1.1171	.0147	.181	1.2233	.0246	.276
				1.3828	.0278	.275
Crude bile salts	0.6524	.1859	3.91	0.6882	. 1998	3.99
	.8930	.2512	3.86	.7282	.2341	4.08

^a Corrected for the sulfuric acid added and the trace in the reagents introduced in the process.

The results in Table I clearly show that the fusion method tends to give low and irregular results. For cystine the values are distinctly low by the fusion method, but the Perhydrol method gives theoretical values and excellent checks. That the low results in the fusion method are due to the loss of sulfur by volatilization is shown by a combustion of a proper mixture of cystine and fusion mixture in a combustion tube with a slow, well-regulated and well-washed current of air passing over the material, and a final washing of the air through 2 wash bottles containing $0.5\,N$ sodium hydroxide solution. The latter solution was next evaporated almost to dryness and analyzed for sulfur by the Perhydrol method. Blank estimations were made in the same way with fusion mixture alone, in the combustion tube instead. By thus heating 2 g. of cystine with 75 g. of fusion mixture and

gradually raising the temperature in the course of $2^{1}/_{2}$ hours, we obtained 2.8% of the cystine sulfur in the washing solution, after due allowance had been made for a careful blank test. This, to be sure, is a rapid heating but repetition of the same experiment with a very gradual heating over a period of 6 hours gave 1.3% of the cystine sulfur in the washing solution. Furthermore, when the gases from the tube at the close of this period were passed into a lead acetate solution, a precipitate of lead sulfide was obtained at once.

The completeness of oxidation of cystine sulfur is easily shown by observation of the rapid loss of reduced sulfur in an alkaline solution of cystine when it is treated with hydrogen peroxide. Such solutions can no longer be reduced to cysteine by sodium sulfite as suggested by Folin and Looney¹⁷ in their recent method for the estimation of cystine. However, such oxidized solutions do not yield calculated values for sulfate unless the alkaline peroxide oxidation is followed by the usual nitric acid and bromine combustion.

Summary

- 1. The dry fusion method used in these studies tends to give low results when properly corrected for blanks.
- 2. These low and irregular results are due to the loss of reduced sulfur by volatilization during the heating period of the dry mixture. This loss is greater the more rapidly the temperature is increased.
- 3. The new Perhydrol method gives calculated values for cystine. The results are uniform and in general higher than by the fusion method on different forms of organically combined sulfur found in biological material.
- 4. Blank estimations for sulfates are made easily and accurately by adding a known amount of sulfate (10 cc. of 0.1 N solution) to the solution in order to hasten the complete precipitation of traces of sulfate.

CHICAGO, ILLINOIS

¹⁷ Folin and Looney, J. Biol. Chem., 51, 427 (1922).

[Contribution from the Department of Chemistry, Columbia University, No. 416]

EFFECT OF AMINO ACIDS IN RETARDING THE HYDROLYTIC DECOMPOSITION OF AN ENZYME (PANCREATIC AMYLASE)

By H. C. Sherman and Florence Walker Received May 14, 1923

In recent work dealing with the effect of amino acids upon the action of amylases we have found that glycine, alanine, tyrosine, phenylalanine, aspartic acid and asparagine exert a favorable influence upon the enzymic hydrolysis of starch.

As more fully described in previous papers, 1,2 the activity of the amylase was measured by the amount of reducing sugar formed when the quantity of enzyme necessary to saccharify about $^{1}/_{5}$ of the substrate acted for $^{1}/_{2}$ hour at 40° on 100 cc. of a 1% dispersion of Lintner "soluble" starch containing optimum amounts of sodium chloride and disodium phosphate. The reducing sugar thus formed, chiefly maltose, was estimated by finding the weight of cuprous oxide precipitated as the result of the action of the digestion mixture on 50 cc. of mixed Fehling solution for 15 minutes in a boiling water-bath.

The carefully neutralized amino acids added to the starch pastes did not alter the hydrogen-ion concentration of the digestion mixtures. The favorable effect upon the activity of the enzyme was most marked in the case of purified pancreatic amylase, the amount of reducing sugar produced by this enzyme being about 15% greater in the presence of any one of the above-mentioned amino acids in a concentration of 0.05%. This enzyme was, therefore, used in the present study, in which a further explanation of the favorable effect of the amino acids was sought.

Experiments have already been reported showing that: (1) the favorable influence of the amino acids cannot be attributed to their combination with some product or products of digestion which, if left free in solution might bring the starch-enzyme reaction to equilibrium, or else react with the enzyme itself, thereby rendering it inactive; (2) the effect is not due to a more favorable hydrogen-ion concentration induced by the presence of the amino acids, since in our experiments an optimum hydrogen-ion concentration was maintained throughout; (3) glycine is markedly effective in counteracting the deleterious influence of cupric sulfate on pancreatic amylase, thus suggesting that the amino acid may act by protecting the enzyme from some unknown injurious substance which may be present accidentally or as a constituent of the substrate or enzyme material; (4) positive evidence has been found that the favorable influence of amino

¹ Sherman and Walker, This Journal, 41, 1867 (1919).

² Sherman and Walker, ibid., 43, 2461 (1921).

acids is due at least in part to the fact that they prevent or retard the deterioration of the amylase in its aqueous solution.

In studying this last point, three methods of investigation have been used: (1) the resulting losses in activity of equal portions of the same enzyme solution were compared after these portions had stood in absence of substrate for a definite length of time at known temperatures, alanine having been added to some portions while others contained no amino acid; (2) the effect of temperature upon "activation" due to amino acids was determined; (3) a similar series of experiments was carried out in which the enzyme was allowed to act at these different temperatures for a longer time.

Protection of Pancreatic Amylase from Hydrolytic Destruction in Absence of Substrate

The enzyme was dissolved in (1) water alone, (2) water and alanine, 0.1%, (3) water with optimum concentrations of sodium chloride and disodium phosphate, (4) water with the same salts plus alanine. Such solutions were allowed to stand for 1 hour, in one series at 22° and in another at 40° , and their enzymic activities then determined, the results being expressed in terms of the weight of cuprous oxide obtained. In the determinations of enzymic activity, alanine was added to those solutions which had not previously contained it so as to have the same concentration of alanine present in all cases during the action of the enzyme upon the starch and the treatment of the resulting solution with the Fehling reagent.

The results are shown in Table I.

Table I $\begin{tabular}{ll} \textbf{Effect of Alanine in Retarding Deterioration of Pancreatic Amylase in Solution at 22° and 40° \\ \end{tabular}$

			Cuprous oxide			
Alanine 0.1%	NaCl Optimum conc.	Na ₂ HPO ₄ Optimum cone,	At 22° Mg.	At 40° Mg.		
absent	present	present	274	144		
present	present	present	275	198		
present	absent	absent	133			
absent	absent	absent	98			

These experiments give direct evidence that the amino acid does retard the hydrolytic destruction of the amylase. Solutions of pancreatic amylase (containing optimum concentrations of sodium chloride and phosphate) which have stood 1 hour at 40° show about 1/3 greater amylolytic activity when alanine has been added to the solution in advance. Under similar conditions except that the solution is kept at 22° instead of 40° there is no measurable difference, probably because the deterioration at this temperature and for this short time in the presence of optimum concentrations of salts is so small in either case that the effect of the amino acid is not demonstrable. Even at this lower temperature, however,

the deterioration of the enzyme in the absence of the salts was very marked and this deterioration was much retarded by the presence of the amino acid.

Effect of Variation of Temperature of Digestion

If protection against hydrolytic destruction explains the increased activity of enzymes in the presence of amino acids, it is logical to expect that conditions favoring the hydrolysis of the enzyme molecule, such as a higher temperature or subjection to a given temperature for a longer period, would increase the difference resulting from the presence of the amino acid. To test this point, a series of experiments was planned in which 30-minute and 60-minute digestions by pancreatic amylase with and without amino acid were carried out at temperatures ranging from 30° to 75°.

Table II

Effect of Temperature on Apparent Activation of Purified Pancreatic Amylase

by Glycine

		Results e	expressed	in terms	of cupro	ıs oxide		
	:	30-minute		of activity		60-minute	digestions Increase o	f activity
Tempera- ature ° C.	Glycine 50 mg. Mg.	e added None Mg.	due to gly Mg.	50 mg. of cine %	Glycin 50 mg. Mg.	e added None Mg.	due to 50 glyci Mg.	
30	155	136	19	14	142	114	28	24
40	252	220	32	14	287	248	39	15
50	366	311	55	17	343	259	84	32
55	393	291	102	35	369	214	155	72
57	363	251	112	45	367	167	200	120
60	380	183	197	107	320	84	236	281
65	176	58	118	203	99	24	75	312
66.5	110	30	80	266	52	19	33	173
70	55	24	31	129	18	8	10	125
75	0	0	0	0	0	0	0	0

TABLE III

Effect of Temperature upon Apparent Activation of Purified Pancreatic Amylase by Phenylalanine

	R	lesults e	xpressed	in terms	of cupror	us oxide		
	30-minute digestions Increase of activity			60-minute digestions Increase of activity				
Tempera- ature °C.	Phenylalanin 50 mg. Mg.	e added None Mg.	due to	phenyl- nine	Phenylal 50 mg. Mg.	anine added None Mg.	due to	
30	183	164	19	12	173	143	30	21
40	291	258	33	12	290	247	43	17
50	340	255	85	33	300	194	106	55
55	291	181	110	60	226	94	132	140
60	134	66	68	103	105	37	68	184
65	42	25	17	68	22	12	10	83
70	10	7	3	43	6	4	2	50

Table II shows the results obtained with glycine at different temperatures when 0.6 cc. of 0.01% enzyme solution acted upon 100 cc. of substrate

for 30 minutes and when $^{1}/_{2}$ the amount acted upon the same amount of substrate for 60 minutes. The experiments were repeated with phenylalanine replacing glycine, the results of which are given in Table III. The purified pancreatic amylase preparation employed in the phenylalanine experiments was about a year older than that used with glycine and only $^{2}/_{3}$ as active; consequently, $^{1}/_{3}$ more of the solution was added to each digestion mixture.

The results of the above experiments afford striking evidence that deterioration of the enzyme with increase in temperature is retarded by amino acids. For the 30-minute digestions, beginning with an increase at 30° of 19 mg. of cuprous oxide or 14%, the favorable influence of glycine reaches a maximum of 197 mg. of cuprous oxide or over 100% at 60° . Above this temperature the effect as represented by increase in milligrams of cuprous oxide declines sharply, although the percentage of apparent activation continues to increase up to 66.5° . The rapid falling off in activity above 60° is doubtless due to coagulation of the amylase which is not prevented by the amino acid.

The experiments with phenylalanine show the same general effect, though not in quite so marked degree as in the case of glycine, perhaps because of the lower molar concentration in which it was used. It will be observed from the tables that the 2 amylase preparations in absence of either amino acid behave somewhat differently, the less active one, employed in connection with phenylalanine, being destroyed more rapidly with increasing temperature. Glycine added to a substrate hydrolyzed by this enzyme at 60° gave practically the same result as obtained with phenylalanine. Hence the lack of perfect agreement in the temperature at which the optimum effect was found is probably due not to dissimilarity in the action of the two amino acids but rather to some difference in the amylase solutions connected with the deterioration which had already occurred in the less active preparation.

The most evident explanation of the marked temperature effect above shown is that the amino acids preserve the enzyme in solution from the destructive influence of hot water. Thus increase in temperature exerts two opposite influences upon amylolytic action. It accelerates the velocity of hydrolysis of starch into sugar by the amylase and at the same time increases the rate of deterioration (presumably hydrolytic destruction) of the enzyme. The second reaction being retarded by the presence of one of its products (amino acids), the first effect, that is increase in the rate of hydrolysis of the starch, becomes more noticeable.

When hydrolysis was continued for 60 minutes the amino acids produced a greater apparent activation at all temperatures (up to that at which coagulation of the enzyme occurred) than was observed in similar experiments of 30 minutes' duration. Digestions carried out at 40° for periods

of time from 20 minutes to 3 hours with and without glycine and tyrosine show the same increase in apparent activation with length of time of action of the amylase. This is what would be expected if the amino acid exerts its favorable influence by protecting against deterioration, since the longer the enzyme is subjected to an injurious temperature, the greater the deterioration and consequently the more apparent becomes the favorable effect of the conserving influence of the amino acid.

Summary and Conclusions

- 1. Highly purified preparations of pancreatic amylase, which deteriorate more rapidly in aqueous solution than the other amylases studied in this Laboratory, are also more affected by the presence of amino acids than are the other enzymes.
- 2. Solutions of pancreatic amylase (containing optimum concentrations of chloride and phosphate) which have stood 1 hour at 40° show considerably greater activity when alanine has been added to the solution in advance. Amylase solutions to which the chloride and phosphate have not been added deteriorate more rapidly; and with these the protective effect of the amino acid can be demonstrated at lower temperatures.
- 3. There is a striking increase in apparent activation by glycine and phenylalanine with increased temperature of digestion until coagulation of the enzyme occurs.
- 4. At the same temperatures there is greater apparent activation when hydrolysis is allowed to proceed for 1 hour than when the action is stopped at the end of 30 minutes.
- 5. All these facts point to the conclusion that the favorable influence of amino acids on the enzymic hydrolysis of starch is due, in large part at least and in all probability mainly, to a protection of the enzyme from deterioration in the aqueous dispersion in which it acts. This deterioration is probably due to gradual hydrolytic destruction.
- 6. That the presence of amino acids retards the hydrolytic destruction of the enzyme constitutes, as we have previously pointed out, an interesting addition to the evidence supporting the view that the enzyme itself is a substance of protein nature or one which contains protein as an essential constituent.

We are greatly indebted to the Carnegie Institution of Washington for grants in aid of the investigation.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE SPONTANEOUS DISSOCIATION OF TRIPHENYLMETHYL DISULFIDE WITH THE FORMATION OF TRIPHENYL-METHYL. THE POTASSIUM DERIVATIVE OF TRIPHENYL CARBINOL AND ITS USE AS A SYNTHETIC AGENT

By F. F. BLICKE

Received May 25, 1923

n-Pentamethylene-S-triarylmethyl-dithio-urethans dissociate spontaneously, in solution, with the formation of triarylmethyls; the latter were isolated in the form of their characteristic peroxides.¹

It has now been found that triphenylmethyl disulfide also dissociates spontaneously, in solution, at ordinary temperature with the formation of triphenylmethyl; thus, when the colorless disulfide is dissolved in benzene the solution, colorless at first, soon assumes the deep yellow color which is characteristic for solutions of this radical. When air is passed into the solution, triphenylmethyl peroxide is precipitated. The rational explanation for the above phenomena is expressed as follows:²

$$\begin{array}{c} 2 \; (C_6H_5)_3C - S - S - C(C_6H_5)_3 \Longrightarrow 2 \; (C_6H_5)_3C - + \; 2 \; - S - S - C(C_6H_5)_3 \\ \downarrow \quad \text{oxygen} \\ (C_6H_5)_3C - O - O - C(C_6H_6)_3 \end{array}$$

A comparison of triphenylmethyl disulfide with triphenylmethyl peroxide, as regards dissociation, is interesting. Wieland³ has shown that triphenylmethyl peroxide dissociates very readily when a xylene solution of the material is heated to the boiling point. The dissociation, in this instance, occurs not between the triphenylmethyl group and oxygen but through the severance of the bond between oxygen and oxygen.

It now seemed desirable to prepare the hitherto unknown thioperoxide, $(C_6H_5)_3C$ —S—O— $C(C_6H_5)_3$, and study its behavior with regard to dissociation. It was thought that this substance might readily be prepared by reaction between triphenylmethyl sulfurchloride⁴ and a metallic derivative of triphenyl carbinol. $(C_6H_5)_3C$ —S—Cl + M—O— $C(C_6H_5)_3$ = $(C_6H_5)_3$ -C—S—O— $C(C_6H_5)_3$ + MCl.

Schlenk and Mair⁵ have reported that the sodium derivative of triphenyl-carbinol may be obtained by the action of metallic sodium upon a large excess of the molten carbinol at 185°. This method, however, is unsatisfactory since it is very difficult to free the hygroscopic sodium compound from the large amount of unchanged carbinol.

- ¹ Blicke, This Journal, 45, 544 (1923).
- ² Judging from the yield of peroxide it seems that only one of the triphenylmethyl groups of the disulfide is obtained in the form of triphenylmethyl.
 - ³ Wieland, Ber., 44, 2550 (1911).
 - 4 Vorländer and Mittag, ibid., 52, 415 (1919).
 - ⁵ Schlenk and Mair, ibid., 44, 1076 (1910).

It was found that metallic potassium reacts readily with triphenyl carbinol when the latter is dissolved in boiling xylene. The potassium derivative which is formed is soluble in hot xylene but quite insoluble in the cold solvent and therefore crystallizes out of the latter quite pure. $2(C_6H_5)_3C - OH + 2K = 2(C_6H_5)_3C - OK + H_2.$

Before undertaking a study of the reaction of the metallic compound with triphenylmethyl sulfurchloride it seemed desirable to study the reactions between the former substance and somewhat simpler compounds. Accordingly, the preparation of various triarylmethyl ethers and esters was attempted by treatment of the potassium compound with alkyl halides and acid chlorides, respectively. The potassium compound reacts readily with methyl iodide, and triphenylmethyl-methyl ether is formed in good yield: $(C_6H_5)_3C-OK+CH_3I=(C_6H_5)_3C-O-CH_3+KI$. By the use of ethyl instead of methyl iodide little or none of the corresponding ethyl ether is formed, providing the reaction is carried out under the same conditions. In this instance, ethylene and triphenyl carbinol represent the reaction products: $(C_6H_5)_3C-OK+C_2H_5I=(C_6H_5)_3C-OH+C_2H_4+KI$.

Benzoyl chloride reacts immediately with the metallic carbinol derivative with the formation of triphenylmethyl benzoate.

When an equivalent amount of triphenylmethyl sulfurchloride, dissolved in benzene, was added to the potassium compound, heat was developed and a red-brown solution resulted. The only crystalline, organic products that could be isolated from the reaction mixture were triphenyl carbinol and triphenylmethyl peroxide. Since a considerable amount of potassium chloride was formed, it seems that triphenylmethyl thioperoxide must have been produced initially; the peroxide may have resulted from the interaction of the thioperoxide and unchanged potassium compound: $2(C_6H_5)_3C-S-O-C(C_6H_5)_3+4(C_6H_5)_3C-OK=3(C_6H_5)_3C-O-O-C (C_6H_5)_3 + (C_6H_5)_3C - C(C_6H_5)_3 + 2K_2S$. This explanation of the formation of the peroxide receives support through the fact that triphenylmethyl sulfurchloride reacts with sodium methylate with the formation of triphenylmethyl-methyl thioperoxide;6 when an excess of the alcoholate was used there resulted only a sulfur-free compound which the above-mentioned investigators suspected was triphenylmethyl peroxide. We have repeated this work and found that the sulfur-free substance was unquestionably peroxide. When the potassium compound of triphenyl carbinol was added to the triphenylmethyl sulfurchloride, in the attempt to avoid an excess of the former substance at any time during the reaction, peroxide was again obtained.

The potassium compound reacts with triphenylchloromethane and it was thought that the resulting product might be triphenylmethyl ether, formed in accordance with the equation, $(C_6H_5)_3C-OK+Cl-C(C_6H_5)_3=$

⁵ Ref. 4, p. 416.

 $(C_6H_5)_3C$ —O— $C(C_6H_5)_3$ + KCl. However, in the examination of the reaction product no ether was found. From the mixture of products formed p-hydroxytriphenyl carbinol was isolated; the latter was probably present in the reaction mixture in the form of its anhydride, diphenyl-quinomethane. It is interesting to compare this result with that obtained by Gomberg⁷ when he attempted to prepare triphenylmethyl ether by the action of silver oxide upon triphenylchloromethane in benzene solution. In this case, also, the desired ether was not obtained and diphenyl-quinomethane was isolated as a product of the reaction. If it is assumed that Gomberg obtained $(C_6H_5)_3C$ —O—Ag as the initial product in his experiment, the two reactions then become comparable.

In addition, it was found that the potassium compound of triphenyl carbinol reacts at once with iodine, phosphorus trichloride and other substances which contain reactive halogen.

Experimental Part

Triphenylmethyl Disulfide.—This compound was readily prepared from triphenyl thiocarbinol according to the method of Vorländer and Mittag;8 the formation of the thiocarbinol, however, does not proceed smoothly. The investigators mentioned were the first to prepare triphenyl thiocarbinol; their method consists in treating triphenylchloromethane with sodium hydrogen sulfide, using ethyl alcohol as a solvent. Unfortunately, the method is not an entirely reliable one and occasionally fails to yield the desired product;9 this is due to the fact that triphenylchloromethane reacts with the ethyl alcohol, used as a solvent, with the greatest ease to form triphenylmethyl ethyl ether. We have been able to prepare the thiocarbinol by the action of potassium hydrogen sulfide on triphenylchloromethane, using benzene as a solvent. The potassium hydrogen sulfide, 10 prepared from 6 g. of potassium, was added to 14 g. of triphenylchloromethane, dissolved in 80 cc. of dry benzene. After the mixture had been shaken for 1 week the reaction mixture was filtered and the solvent allowed to evaporate. The slightly gummy product thus obtained was converted directly into triphenylmethyl sulfurchloride and then into the disulfide. The yield of the sulfurchloride compound, based on triphenylchloromethane, never exceeded 50% of that calculated.

Dissociation of the Disulfide.—A solution of 2.7 g. of the disulfide in 15 cc. of dry benzene immediately became deep yellow, the color of dissolved triphenylmethyl. A fairly rapid stream of dry air was passed through this solution and the escaping air was led into aqueous potassium hydroxide. The benzene solution soon became cloudy and after 1 hour quite a heavy precipitate had formed. After 8 hours the precipitated material was separated, washed with hot carbon disulfide and quickly recrystallized from toluene. The compound thus obtained melted at 185°; mixed with triphenylmethyl peroxide, prepared from triphenylchloromethane and molecular silver, the melting point of the mixture was found to be 185–186°. The yield of peroxide was 0.82 g. The alkaline solution was found to contain potassium sulfite, thus showing that sulfur dioxide had also been formed during the reaction.

In another experiment, 2.25 g. of the disulfide, dissolved in 10 cc. of benzene, was used. After air had been passed through the solution for 1 hour no peroxide appeared

⁷ Gomberg, This Journal, 35, 202 (1913).

⁸ Vorländer and Mittag, Ber., 46, 3453 (1913).

⁹ Mittag, Dissertation, Halle, 1915.

¹⁰ Bloxam, J. Chem. Soc., 77, 758 (1900).

but the latter soon settled out of the solution when the sides of the containing flask were rubbed with a stirring rod; yield of peroxide, after 12 hours, 0.70 g.

Potassium Derivative of Triphenyl Carbinol.—A mixture of 11.5 g. of pure, dry triphenyl carbinol and 100 cc. of xylene, which had previously been refluxed over metallic sodium and then distilled, was put into a 500cc. round-bottom, 3-neck flask. The latter was fitted with a reflux condenser, which was closed with a soda-lime tube, and an inlet tube. After the air in the flask had been displaced by dry nitrogen 1.5 g. of potassium was added; the mixture was then refluxed, enough heat being applied to keep the xylene boiling fairly vigorously. A continuous stream of nitrogen was passed through the flask. After 3 to 4 hours the potassium had practically all disappeared. As the clear, hot solution cooled, the potassium compound precipitated at once in the form of colorless, transparent crystals. After 12 hours the supernatant liquid was decanted and the crystalline material removed from the flask. During the latter operation the material was protected from atmospheric moisture by a stream of nitrogen; yield of crystals, about 10 g.

When the transparent crystals were heated to 220°, under 20 mm. pressure, an amount of xylene was evolved that corresponded to about 21% of the weight of the original material; calcd. loss for 1 molecular equivalent of xylene, 25%. The material, which did not melt during this process, was converted into an opaque, granular substance. For the purposes of synthesis it is not necessary to free the potassium compound from xylene.

When exposed to the air the crystalline product is quickly converted into a powder. Contact with moisture changes the material to triphenyl carbinol and potassium hydroxide; a weighed portion of the xylene-free compound was thrown into water, the resulting potassium hydroxide estimated and was found to be 93.4% of the calculated amount. The low result is due to the fact that a small amount of carbinol, which was used in slight excess in the preparation of the compound, always settles out of the xylene.

Reaction with Methyl Iodide.—A mixture of 10 g. of the potassium compound (the material containing xylene of crystallization was used in this and in all subsequent experiments), 12 g. of pure methyl iodide and 30 cc. of dry benzene was gently refluxed for 2 hours, then poured into an evaporating dish and, after the solvent had evaporated, the crystalline residue was washed with water until free from potassium iodide. The dried material was boiled with 50 cc. of petroleum ether (80–100°) and then filtered. The first crop of crystals which appeared upon cooling proved to be carbinol, later the methyl-triphenylmethyl ether crystallized in pure condition. The substance melts at 83–4° as given in the literature. Yield 6 g., or 82% of the calculated amount.

Reaction with Ethyl Iodide.—Ten g. of the potassium compound, 12 g. of ethyl iodide and 30 cc. benzene were refluxed for 2 hours in a 100cc. flask. The gas evolved during the reaction amounting to 480 cc. (N. T. P.) was collected over water, backward diffusion of moisture into the reaction flask being prevented by a calcium chloride tube, and proved to be ethylene by converting it into ethylene bromide and identification of the latter by its melting and boiling points. The amount of ethylene found corresponds to 78% of that calculated. 7.0 g. of triphenyl carbinol was obtained; calc., 6.9.

Reaction with Benzoyl Chloride.—A mixture of 8 g. of the potassium compound, 3.8 g. of carefully purified benzoyl chloride and 30 cc. of benzene reacted immediately with considerable evolution of heat, moisture having been carefully excluded. After

A trace of unchanged potassium often remains mixed with the potassium compound. It is advisable, therefore, to treat the reaction mixture as described above; during the evaporation of the solvent the atmospheric moisture reacts with the potassium and the solid residue may then safely be treated with water.

¹² Hemilian, Ber., 7, 1208 (1874). Straus and Hüssy, ibid., 42, 2176 (1909).

24 hours the reaction mixture was poured into an evaporating dish, the solvent was removed and the organic matter was extracted with hot benzene. The benzene solution was concentrated under reduced pressure; triphenylmethyl benzoate separated from the cold, coned. solution in good yield. The compound was further purified by recrystallization from a mixture of chloroform and petroleum ether. The ester melts at 165–166°.

For the purpose of comparison the ester was prepared by another method: $4 \, \mathrm{g}$, of triphenylchloromethane, $6.5 \, \mathrm{g}$. of silver benzoate and $50 \, \mathrm{cc}$. of benzene were heated to $60 \, \mathrm{°}$, for 4 hours, in a bath. After the benzene had been removed from the reaction mixture by evaporation, the organic material was recrystallized twice from benzene. The ester, prepared by this method, melted at $165-166 \, \mathrm{°}$.

One g. of the ester was hydrolyzed quantitatively by boiling for 1 hour with 30 cc. of water containing a few drops of sulfuric acid.

Reaction with Triphenylmethyl Sulfurchloride.—A mixture of 8 g. of the potassium compound, suspended in 30 cc. of benzene, with an equivalent amount of triphenylmethyl sulfurchloride dissolved in the same solvent, became warm, and after standing for 24 hours protected from moisture the clear, red-brown solution was poured into an evaporating dish. The presence of a gelatinous, transparent precipitate, presumably colloidal potassium chloride, which was obtained in all of the reactions, made filtration of the reaction mixture impossible. After spontaneous evaporation of the benzene the residue was treated with dry ether; from the latter triphenyl carbinol was obtained. The etherinsoluble residue was washed with water to remove potassium chloride, dried, and then dissolved in a small amount of boiling toluene. As the solution cooled, triphenylmethyl peroxide was obtained.

Reaction with Triphenylchloromethane.—Equivalent amounts of triphenylchloromethane and the potassium derivative of the carbinol, suspended in benzene, were shaken in a sealed tube. After 4 hours the mixture was deep red and after 4 days the contents of the tube consisted of a heavy gelatinous precipitate and an orange-colored liquid. Absolute ether was added and the mixture was filtered; the filtrate was then heated under diminished pressure until the solvent was removed. The residue, which consisted of crystals and an orange-colored oil, was dissolved in acetone and, after the addition of 5% sodium hydroxide solution, was heated on a steam-bath until all of the acetone had evaporated. After filtration from alkali-insoluble material the filtrate was concentrated to a small volume; flaky crystals, possessing a pearly luster, were formed as the solution stood. This material was the sodium salt of p-hydroxytriphenyl carbinol. It was converted into both the colorless benzenoid and the yellow quinonoid forms of the hydroxycarbinol. When the yellow form of the carbinol was heated at 110° for several hours the brown-yellow fuchsone resulted; after several recrystallizations from benzene and petroleum ether this melted at $166-167^{\circ}$.

Summary

- 1. Triphenylmethyl disulfide dissociates spontaneously, in solution, at ordinary temperature with the formation of triphenylmethyl; the latter was isolated in the form of its peroxide.
- 2. The potassium derivative of triphenyl carbinol was prepared. It reacts with alkyl halides to form ethers and with acid chlorides to form esters. In some instances, however, the potassium compound reacts abnormally.

ANN ARBOR, MICHIGAN

¹³ Gomberg, This Journal, 35, 1037 (1913).

¹⁴ Bistrzycki and Herbst, Ber., 36, 2335 (1903).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

HYDROXYNAPHTHOQUINONE STUDIES. VI. THE CHLORINATION OF JUGLONE

By Alvin S. Wheeler, P. R. Dawson and Joseph L. McFwen Received June 7, 1923

The first work on the chlorination of juglone was done by Wheeler and Scott¹. They reported that the chlorination of juglone in cold glacial acetic acid solution gave juglone dichloride, an addition product, which lost hydrochloric acid by the action of hot alcohol, giving a monochloro substitution product. On the other hand the chlorination of juglone in

Chlorination of Juglone

hot acetic acid solution gave a dichlorojuglone which is a substitution product. The latter reaction was further studied by Wheeler and Dawson and several derivatives were made but the results were not published on account of incompleteness. They are now incorporated in this paper.

¹ Wheeler and Scott, This Journal, 41, 833 (1919).

They consisted briefly in the benzoylation of dichlorojuglone; the preparation of the sodium salt which was found to dye silk and wool fabrics certain buff shades readily; the alkylation of dichlorojuglone in which 1 chlorine atom was replaced by the aniline radical and finally the replacement of 1 chlorine atom by the hydroxyl group under the influence of hot alcoholic sodium hydroxide and the acetylation of this product. The work just carried out includes the alkylation of dichlorojuglone with p-chloro-aniline and p-toluidine; the reduction of dichlorojuglone with zinc and sulfuric acid and acetylation of this product; the reaction of sodium ethylate and attempts to prepare an oxime.

The chlorination of juglone was studied under various conditions. No chlorination was found to take place in carbon tetrachloride solution but it proceeded smoothly in glacial acetic acid. Scott passed chlorine in for 3 hours; Dawson reduced the time somewhat but McEwen finds 2 hours to be best.

In one preparation a very unexpected result was obtained, the whole product being a green amorphous substance. A compound of similar appearance and properties was obtained by Mylius² by boiling juglone with water. To determine whether the chlorine was concerned in the reaction we dissolved the juglone in hot acetic acid and set the solution aside overnight. The same amorphous green product was obtained. It was insoluble in the usual organic solvents, did not melt at 310° and dissolved in alkalies giving a deep violet solution. The formula of Mylius, $C_{20}H_{10}O_{7}$, suggests that oxidation of juglone has occurred with the condensation of two molecules to produce a peroxide:

The chlorine atoms in dichlorojuglone according to our belief are located at Positions 2 and 3. Whether we accept the Thiele Partial Valence theory, the Bamberger theory³ or the Willstätter formula⁴ for the constitution of naphthalene, the Positions 2 and 3 in juglone are reactive ones and substitution should readily take place there. For a time we thought that 1 chlorine atom might enter Position 8, since this is a phenol ring and the hydrogen at Position 8, para to the hydroxyl, would be reactive. However, our experiments show that 1 chlorine atom is more reactive than the other, being driven out of the molecule not only by strong bases such as sodium hydroxide but also by weak bases such as aniline and p-chloroaniline. In this connection it is interesting to note that as soon as 2 chlorine atoms are present in the aniline molecule, its basicity is so far

² Mylius, Ber., 18, 463 (1885).

³ Bamberger, Ann., 257, 49 (1890) and following papers.

⁴ Willstätter, Ber., 44, 3430 (1911).

reduced that it has no effect upon the dichlorojuglone molecule. If the 2 chlorine atoms are at Positions 2 and 3 we observe that the quinone ring is surcharged with negativity, having all 4 Positions occupied by oxygen or chlorine. It is very easy to believe that in such an environment 1 chlorine atom may be easily displaced.

In view of the fact that juglone readily takes up 3 bromine atoms, it is very peculiar that under the same conditions only 2 chlorine atoms enter the molecule, and a special attempt failed to introduce a third.

Attention is called to the color phenomena shown by the hydroxychlorojuglone. This compound dissolves in water, giving a deep red solution but if even a slight amount of acid is added, the solution becomes yellow. On neutralization of the acid, the red color reappears.

Experimental Part

The Chlorination of Juglone.—In order to arrive at the best conditions for the chlorination of juglone, carbon tetrachloride and glacial acetic acid were compared as media. There seemed to be little or no action in carbon tetrachloride solution but chlorination in acetic acid proceeded very smoothly. The time of passing in the chlorine and the subsequent heating were varied and the following procedure was finally adopted as best.

Two g. of juglone was dissolved in 20 cc. of glacial acetic acid and placed in a test-tube immersed in hot water. Chlorine, prepared by the action of hydrochloric acid on potassium permanganate and purified by passing through water, sulfuric acid and phosphorus pentoxide, was passed into the solution slowly for $1^3/_4$ hours and then rapidly for 20 minutes. As the solution cooled a mass of orange-red needles separated, the first crop weighed 1.82 g., a pure product; m. p., 149° . The second crop, obtained by concentrating the mother liquor, weighed 0.56 g.; m. p., 138° .

Owing to the easy formation of tribromojuglone, some attempts were made to introduce a third chlorine atom. Chlorine was passed into the hot solution more rapidly and for a longer time. The product consisted of less well defined crystals that were more compact, redder in color and more soluble in acetic acid and other solvents. The melting point was considerably lower, 110–116°, and was very slowly raised by repeated recrystallizations. The determination for chlorine gave a surprising result, the percentage being only slightly above that for dichlorojuglone. This reaction will be re-examined.

Sodium Salt of Dichlorojuglone. 5 —A solution of 1.4 g. of dichlorojuglone in 300 cc. of ether was shaken with 30 cc. of a 10% solution of sodium carbonate for 30 minutes. After the mixture had stood for some time the ether layer was removed and the dark colored precipitate in the water layer was filtered off. The sodium carbonate was washed out with small portions of cold water. The dry salt has an indigo-blue color and is somewhat soluble in alcohol. The aqueous solution has a deep violet color. Acidification liberates dichlorojuglone.

⁵ Work of P. R. Dawson.

Analysis. Subs., 0.3394: Na₂SO₄, 0.0841. Calc. for C₁₀H₅O₅Cl₂Na: Na, 8.68. Found: 8.01.

The preparation of the salt by adding sodium hydroxide to an alcoholic solution and precipitating with sodium chloride was less satisfactory owing to the difficulty of getting rid of the sodium chloride.

The sodium salt may be used for dying silk and wool shades of buff and brown. When, for example, silk is heated in such a solution the deep violet color soon turns to yellowish brown and the silk is dyed an attractive buff shade, fairly fast to light.

2,3-Dichloro-5-benzoxy-1,4-naphthoquinone,⁵ C₁₀H₅O₂.Cl₂.OCOC₆H₅.—A solution of 0.5 g. of dichlorojuglone in 5 cc. of benzoyl chloride was heated to boiling for 3 hours. The color changed from red to brown. Evaporation of the liquid gave a product weighing 0.64 g. which after several recrystallizations from benzene melted at 225°. It forms light yellow needles, slightly soluble in alcohol, acetone and moderately soluble in benzene.

Analysis. Subs., 0.1588: AgCl, 0.1320. Calc. for C_1 : $H_5O_4Cl_2$ (347): Cl, 20.46. Found: 20.53.

2,5-Dihydroxy-3-chloro-1,4-naphthoquinone, ⁵C₁₀H₃O₂(OH)₂Cl.—A mixture of 2.0 g. of dichlorojuglone, dissolved in 160 cc. of warm alcohol, and 80 cc. of 10% sodium hydroxide was boiled for 1 hour. The deep violet solution soon changed to dark red and a small amount of precipitate appeared. The mixture was poured into 200 cc. of cold water, and the precipitate dissolved. Upon acidification with hydrochloric acid an abundant separation of very fine yellow needles took place. This product weighed 1.45 g.; m. p., 188–189°. A second crop weighed 0.22 g.; m. p., 181–183°. The substance is extremely soluble in alcohol, slightly so in ligroin and fairly soluble in water, giving a deep red solution. The pure substance, m. p., 191°, is obtained by recrystallizing several times from dil. alcohol. The crystals are needles which are red when wet and golden-brown when dry.

Analysis. Subs., 0.1661: AgCl, 0.1062. Calc. for $C_{10}H_{6}O_{4}Cl$ (224.5): Cl, 15.81. Found: 15.83.

As stated above, the neutral solution in water is deep red. Addition of a slight amount of acid changes it instantly to yellow and neutralization restores the red color. Crystals obtained from the 2 solutions are identical in form and melting point.

2,5-Diacetoxy-3-chloro-1,4-naphthoquinone, 5 C₁₀H₃O₂Cl(OCOCH₃)₂.—A solution of 0.5 g. of the hydroxy derivative in 8 cc. of acetic anhydride was gently boiled for 8 hours. The color gradually changed from dark red to yellow-brown. The product, precipitated by the addition of cold water, weighed 0.62 g. and melted at 142–143°. On recrystallization twice from alcohol the pure substance is obtained in beautiful, fine yellow needles, melting sharply at 147°.

Analyses. Subs., 0.2509, 0.1908: AgCl, 0.1187, 0.0895. Calc. for $C_{14}H_9O_6Cl$ (308.5): Cl, 11.51. Found: 11.72, 11.64.

2-Anilino-3-chloro-5-hydroxy-1,4-naphthoquinone,⁶ C₁₀H₃O₂.NHC₆H₅.Cl.OH.— A solution of 1 g. of dichlorojuglone in 75 cc. of alcohol was added 0.4 g. of aniline (slightly in excess of 1 molecular equivalent). The reaction began at once, and the solution became deep violet-red. The mixture was boiled for 15 minutes and then cooled. Very small, short, flat needles separated in abundance. Viewed in the mass they have a violet-carmine color with a metallic luster. Under the microscope they appear to resemble chips of pine bark because of their color and the jagged ends. The first crop weighed 0.9 g., m. p., 218–221°. A second crop weighed 0.22 g. Recrystallization from

Work of Dawson and McEwen.

acetone raised the melting point to 222°. The substance is fairly soluble in alcohol, very soluble in benzene and best purified from acetone.

Analysis. Subs., 0.1524: AgCl, 0.0726. Cale. for $C_{16}H_{10}O_3NCI$ (296.6): Cl, 11.83. Found: 11.88.

An attempt was made to carry out the reaction with 2,4-dichloro-aniline but even after it had been heated all day the dichlorojuglone was recovered unchanged. *p*-Monochloro-aniline reacted easily, as described below.

2-p-Chloro-anilino-3-chloro-5-hydroxy-1,4-naphthoquinone, 7 $C_{10}H_3O_2$.NHC $_6H_4$ Cl.-Cl.OH.—To a solution of 1 g. of dichlorojuglone in 75 cc. of hot alcohol, 0.53 g. of p-chloro-aniline was added, and the mixture was boiled for 30 minutes, the color turning to a dark brownish-red. As the solution cooled 0.8 g. of the product crystallized out. It consisted of dark reddish-purple, flat needles with jagged ends, that melted at 237°. The pure substance, obtained by recrystallization from acetone, melted at 243°. The substance is easily soluble in benzene, and moderately soluble in alcohol or ether.

Analysis. Subs., 0.1765: AgCl, 0.1530. Cale. for $C_{16}H_9O_3NCl_2$ (334): Cl, 21.33. Found: 21.45.

2-p-Toluino-3-chloro-5-hydroxy-1,4-naphthoquinone, 7 C₁₀H₃O₂.NHC₆H₄CH₃.Cl.OH. —An alcoholic solution of 1 g. of dichlorojuglone and 0.44 g. of p-toluidine was boiled for several minutes. Crystals began to appear before boiling commenced. The first crop of crystals weighed 0.8 g. These were dark, reddish-purple, flat needles with jagged ends and a brilliant luster. Recrystallization from acetone gave a pure product melting at 234° .

Analysis. Subs., 0.1560: AgCl, 0.0723. Calc. for $C_{17}H_{12}O_2NCl$ (313.6): Cl, 11.31. Found: 11.46.

1,4,5-Trihydroxy-2,3-dichloronaphthalene, $^7C_{10}H_3(OH)_3Cl_2$.—To a suspension of 2 g. of dichlorojuglone in 50 cc. of ether were added some sulfuric acid (1:5) and zinc dust in small portions at short intervals, while the mixture was well shaken. As the dichlorojuglone was reduced it was taken up by the ether which became faintly yellow. The ether was separated, washed well with water and allowed to evaporate at room temperature. The residue was a mass of gray crystals with a metallic luster, resembling aluminum powder. The product weighed 2.0 g. and melted at 154–156° with decomposition. It was purified by dissolving it in alcohol and adding water until crystallization began. The pure product consisted of very small short prisms, gray in the mass with a brilliant metallic luster, and melting at 157° with decomposition. There is danger of decomposing the compound in the purifying process. We lost two small lots which became nearly black. It is readily soluble in acetone and in ether, difficultly soluble in hot benzene and insoluble in ligroin.

Analysis. Subs., 0.1771: AgCl, 0.2085. Calc. for $C_{10}H_6O_3Cl_2$ (245): Cl, 28.98. Found: 29.12.

1,4,5-Triacetoxy-2,3-dichloronaphthalene, 7 $C_{10}H_3(OCOCH_3)_3Cl_2$.—A solution of 1 g. of the reduction product in 15 cc. of acetic anhydride was boiled for 12 hours, soon turning yellow. Evaporation of the liquid gave a product melting at 165–170°. After recrystallization from alcohol it melted at 182° and consisted of well developed, transparent needles that were light yellow when viewed in the mass. The substance is easily soluble in acetone, fairly soluble in benzene and alcohol and nearly insoluble in ether.

Analysis. Subs., 0.1535: AgCl, 0.1196. Calc. for C₁₆H₁₂O₆Cl₂(372): Cl, 19.06. Found: 19.27.

Reaction with Sodium Ethylate. From an equivalent molecular mixture of di-

⁷ Work of McEwen.

chlorojuglone and freshly made sodium ethylate a dark purple precipitate formed immediately (in benzene solution). When this was dissolved in water and acidified with hydrochloric acid, the solution turned yellow and a yellow precipitate formed. This proved to be the hydroxychlorojuglone, m. p., 191°, described above. It showed the same color phenomena. We had hoped to find also an ethoxy derivative of dichlorojuglone.

Attempt to Prepare an Oxime.—One g. of dichlorojuglone was dissolved in 20 cc. of alcohol containing 0.3 g. of hydroxylamine hydrochloride (1 molecular equivalent), and 2 drops of strong hydrochloric acid. After the solution had boiled for 2 hours and then cooled, a product was obtained, but it contained no nitrogen and proved to be unchanged dichlorojuglone. The experiment was tried with 2 molecular equivalents of the hydroxylamine salt and boiling was continued for 8 hours, but with no better success.

Summary

- 1. The best method of chlorinating juglone is described.
- 2. A description of the sodium salt and the benzoate of dichlorojuglone is given.
- 3. One chlorine atom of dichlorojuglone is replaced by hydroxyl by the action of alcoholic sodium hydroxide. This hydroxyl derivative and its acetate are described.
- 4. Dichlorojuglone was arylated by weak bases such as aniline, p-chloro-aniline and p-toluidine but not by dichloro-aniline. In each case 1 chlorine atom is replaced.
- 5. Dichlorojuglone was reduced in acid solution with zinc, giving a trihydroxynaphthalene. The triacetoxy derivative was also prepared.
- 6. Sodium ethylate yields an hydroxy derivative of dichlorojuglone and not an ethoxy.
 - 7. Hydroxylamine hydrochloride does not give an oxime.
 - 8. Reasons are given for locating the chlorine atoms at Positions 2 and 3. Chapel Hill, North Carolina

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE MECHANISM UNDERLYING THE REACTION BETWEEN ALDEHYDES OR KETONES AND TAUTOMERIC SUBSTANCES OF THE KETO-ENOL TYPE

By E. P. Kohler and B. B. Corson Received June 9, 1923

The discovery that aldehydes and ketones can be condensed with aceto-acetic ester, cyano-acetic ester, diketones, and other substances containing active hydrogen, was a natural consequence of the use of reactions which are supposed to involve aldol condensation for the synthesis of unsaturated compounds. The reagents are not essentially different from those used in these earlier syntheses, the catalysts used to induce reaction are, for the most part, the same, and the two processes usually give the same type of unsaturated compound. Most chemists, doubtless, therefore

assume that the mechanism of the two reactions is also the same, namely, aldol condensation followed by loss of water.

Other views have, however, also been expressed. Knoevenagel, who substituted primary and secondary amines for the sodium alcoholate which had previously been used as the condensing agent, accounted for the catalytic action of the amines by the mechanism:

$$RCHO + 2R_2NH \Longrightarrow RCH = (NR_2)_2 + H_2O$$

$$RCH(NR_2)_2 + H_2C < \longrightarrow RCH = C < + 2R_2NH$$
(2)

In support of this mechanism he showed that hydrobenzamide can be used in place of benzaldehyde and ammonia, and Schiff bases in place of the corresponding aldehydes and amines. It is now known,² however, that tertiary amines can serve as catalysts in these condensations even though they are incapable of reacting with aldehydes and ketones in the manner predicated by Knoevenagel.

A mechanism of an entirely different type was first proposed by Rogerson and Thorpe³ when they found that sodium cyano-acetic ester can be condensed with aceto-acetic ester and with its monomethyl derivative, but not with dimethyl aceto-acetic ester. Since the possibility of condensation here appears to be related to the capacity for enolization, they assume that the metallic derivative is condensed with the enolic modification of the ketonic ester. $CH_3C(OH)=CHCOOC_2H_5+HC(Na)(CN)CO_2C_2H_5$ \longrightarrow H_2O + $CH_3C=CHCOOC_2H_5$

$$H_2O + CH_3C = CHCOOC_2H_5$$

$$C(Na)(CN)CO_2C_2H_5$$

Harding, Haworth and Perkin⁴ adopted this view to account for the fact that they obtained, mainly, a β,γ unsaturated ester when they condensed cyclohexanone and cyano-acetic ester in the presence of either sodium methylate or piperidine. Extending Thorpe's mechanism to ketones which at best enolize but little, and to reactions in which amines are used as condensing agents they interpret their results as follows:

Thorpe's mechanism implies that only aliphatic ketones can be condensed with cyano-acetic ester, and that β,γ unsaturated compounds are the primary products in these condensations. In its support, Haworth⁵ showed, shortly afterwards, that benzophenone failed to react at all under

- ¹ Knoevenagel, Ann., 281, 25 (1894).
- ² Hann and Lapworth, J. Chem. Soc., 85, 46 (1904).
- ³ Rogerson and Thorpe, ibid., 87, 1685 (1905).
- ⁴ Harding, Haworth and Perkin, J. Chem. Soc., 93, 1943 (1908).
- ⁵ Haworth, ibid., 95, 480 (1909).

conditions in which a variety of ketones that are capable of enolization are condensed with great ease.

The latest exposition of this mechanism is contained in a lengthy discussion by Ingold⁶ on the condensation of ketones and aldehydes with the sodium derivative of cyano-acetic ester. The point of view on which this discussion is based is given in the following passage:

"... there can be no doubt but that it is the enolic modification of the ketone which actually enters into the reaction because ketones, such as benzophenone of which no enolic modification can exist, fail to react, while others condense with a readiness apparently proportionate to their capacity for tautomeric change."

To the reasons for holding this view which had been given by others Ingold now adds the general statement that ease of condensation is apparently related to capacity for tautomeric change. He realizes that this is inconsistent with the extraordinary ease with which aldehydes—especially aromatic aldehydes which are incapable of enolization—enter into the reaction, but disposes of the difficulty by suggesting that these may react in a tautomeric form containing bivalent carbon, as, for example, C_6H_5 —C—OH.

The view that these condensations involve the enolization of aldehydes or ketones seemed to us improbable on a variety of grounds. We could find no reasons for assuming that the reactions with cyano-acetic ester are in any way different from those with other substances containing active hydrogen atoms. The formation of β, γ unsaturated compounds in certain special cases can be explained in other ways. The relative ease with which aldehydes and the various ketones enter into the reaction seems to be adequately accounted for by the known differences in the activity of these substances in addition reactions. Thus the well known measurements of Stewart⁸ and of Zelinskey⁹ show that all aldehydes combine with other substances more rapidly than does any ketone; that acetone, aceto-acetic ester and cyclic ketones, like cyclohexanone, combine more rapidly than other ketones; and that benzophenone combines more slowly than any except the most highly substituted aliphatic ketones. The relative activity of these substances in condensation and in addition reactions is, therefore, approximately the same.

Inasmuch as there are carbonyl compounds that are incapable of enolizing and yet combine fairly readily with other substances, it ought to be possible to determine definitely whether enolization is involved in these condensations or not. The two most promising substances for this purpose are the esters of mesoxalic and benzoylformic acids. The

⁶ Ingold, ibid., 119, 329 (1921).

⁷ Lapworth in a recent paper has adduced evidence that the ester obtained by Harding, Haworth and Perkin is probably an α, β -unsaturated compound.

⁸ Stewart, J. Chem. Soc., 87, 185 (1905).

⁹ Petrenko-Kritschenko, Ann., 341, 150 (1905).

condensation of mesoxalic ester and cyano-acetic ester was studied by Schmitt. In the presence of piperidine he obtained along with more complex products a substance whose structure he did not succeed in establishing, but which doubtless was the unsaturated condensation product, $(C_2H_5O_2C)_2C:C(CN)CO_2R$.

We have used methyl benzoylformate and have found that under the influence of sodium methylate, ammonia, methyl amine, aniline and piperidine, methyl cyano-acetate condenses with it in the same way and almost with the same ease that it condenses with aldehydes. The product is the unsaturated compound, II.

$$\begin{array}{cccc} C_6H_5C(OH)CO_2CH_3 & & C_6H_5CCO_2CH_3 \\ & & & & & & \\ CH(CN)CO_2CH_3 & & & C(CN)CO_2CH_3 \\ & & & & & & \\ I & & & & & \\ \end{array}$$

Using the same condensing agents but operating under different conditions it is possible to get as the principal product the saturated hydroxyl compound, I.

With these facts established there remains no reason for assuming that either the reaction between aldehydes or ketones and substances which have active hydrogen, or aldol condensation involves the enolization of aldehydes or ketones.

The addition product (I) is a stable substance. When it is perfectly pure it neither readily loses water nor reverts to its components. Thus, when it is dissolved in pure boiling methyl alcohol or acetone it causes an elevation corresponding to its molecular weight and the solutions can be boiled for hours without further change in the boiling point. When it is heated under very low pressures it partly distils, partly dissociates into its components. Efficient dehydrating agents, however, eliminate water. Thus when it is heated with phosphorus pentachloride in phosphorus oxychloride or digested with glacial acetic acid it passes smoothly into the unsaturated ester (II). Since none of this unsaturated ester is obtained when a mixture of equivalent quantities of the two components is treated in the same way, it must here be formed by loss of water from the hydroxy ester.

The addition product is exceedingly sensitive to bases, disappearing more or less rapidly in the presence of any of the condensing agents used in its synthesis. Thus, when it is added to boiling methyl alcohol or acetone containing relatively very small quantities of any of these bases the boiling point steadily rises and when it finally becomes constant, the elevation corresponds to a molecular weight that is much too small. The solution now contains dimethyl malonate, and methyl benzoylformate as well as addition product; no unsaturated compound could be isolated from it. When solutions of the addition product, containing a larger quantity of these

¹⁰ Schmitt, Ann. chim., [8] 12, 408 (1907).

bases are boiled or, better, when the solid addition product is suspended in a little of these solvents containing a small quantity of base, and the mixture is kept at the ordinary temperature it gradually passes into the unsaturated compound. These relations are most plausibly expressed by the following scheme:

$$\begin{array}{c} C_{6}H_{5}COC_{2}CH_{3} & \longleftarrow \\ CH_{2}(CN)CO_{2}CH_{3} & \longleftarrow \\ I & \downarrow \\ C_{6}H_{5}COC_{2}CH_{3} & \longleftarrow \\ I & \downarrow \\ C_{6}H_{5}COC_{2}CH_{3} & \longleftarrow \\ I & \downarrow \\ C_{6}H_{5}C-CO_{2}CH_{2} & + H_{2}O \\ & \downarrow \\ C_{6}H_{5}C-CO_{2}CH_{3} & \longleftarrow \\ I & \downarrow \\ C_{6}H_{5}C-CO_{2}CH_{3} & \longleftarrow \\ C_{6}H_{5}C-CO$$

If this scheme correctly represents the mechanism by which the unsaturated ester is formed, then the basic condensing agents that are constantly employed in the synthesis of α,β unsaturated compounds fulfil a 2-fold function; they bring about condensation, and they cause elimination of water. There is, however, at present, no proof that the hydroxy ester is an intermediate product in the formation of the unsaturated compound, just as there is no satisfactory evidence that the analogous reactions which are used in the synthesis of unsaturated aldehydes and ketones really involve aldol condensation. Inasmuch as the addition product in the presence of bases reverts to an equilibrium with its components, it is impossible, in the absence of all accurate knowledge of the kinetics of the reaction, to determine whether the unsaturated ester is formed by loss of water from the addition product or directly from the components by some other path. This phase of the matter is still under investigation and will be considered in a later paper.

There is nothing peculiar in the condensations with cyano-acetic esters. Dimethyl malonate behaves in precisely the same way. The addition product is less soluble, and therefore a little more easily got; the residual hydrogen in the malonic ester residue is less active than that in the cyano ester, hence the addition product loses water less readily, and as the resulting unsaturated compound is a liquid it is more difficult to get it as a direct product of condensation. These are only such minor differences as are to be expected. The course of the reaction is the same: probably addition-equivalent to aldol condensation-followed by loss of water. It is safe to assume, therefore, that all condensations between aldehydes or ketones and substances containing active hydrogen occur in this manner.

Experimental Part

Preparation of Materials

Benzovlformic Acid.—The acid was made by the oxidation of acetophenone as directed by Claus¹¹ as well as by the oxidation of mandelic acid by the method of Acree. 12 We prefer the latter; it is more convenient,

11 Claus and Neukranz. J. prakt. Chem., [2] 44, 77 (1891). Kailan, Monatsh., 28,

12 Acree, Am. Chem. J., 50, 389 (1913). Evans, ibid., 35, 115 (1906).

less expensive and more easily conducted on a large scale. Probably the best method for getting pure acid from residues which, owing to the presence of water or small quantities of benzoic acid, are reluctant to crystallize, is distillation under diminished pressure. In a good vacuum the pure acid distils practically without decomposition—the boiling point being about 148° at 4–6 mm. The oily residues distilled at 145–149° at 4–6 mm.; the distillate was colorless and solidified promptly. When the quantity distilled was not too great there was no evidence of decomposition until near the very end of the distillation.

Methyl Benzoylformate.—Claisen¹³ states that the esters of benzoylformic acid are readily made by saturating alcoholic solutions of the acid with hydrogen chloride, but he usually made them from benzoyl cyanide. He gives $246-248^{\circ}$ as the boiling point of the methyl ester. Our first preparation made from the acid and methyl alcohol, boiled at 257° —nearly 10° above the point given by Claisen. As it proved to be unexpectedly resistant to condensation, it was analyzed and found to be the acetal, $C_6H_5C(OCH_3)_2CO_2CH_3$.

Analyses. Calc. for C₁₁H₁₄O₄: C, 62.8; H, 6.7. Found: C, 63.1, 62.5; H, 6.7, 6.2.

Other preparations by the same method gave products composed largely of the ketonic ester, but in order to avoid all possible complications nearly all condensations were first carried out with ester that was made through the silver salt.

II. Condensation of Methyl Benzoylformate and Methyl Cyano-acetate

It was stated in the introduction that the equilibrium, $C_6H_5COCO_2CH_3$ + $CH_2(CN)CO_2CH_3$ \Longrightarrow $C_6H_5C(OH)CO_2CH_3$, is established with ex-

CH(CN)CO₂CH₃

traordinary rapidity. The evidence for this statement is as follows. When a few drops of a saturated solution of sodium methylate in methyl alcohol is added to a mixture of equivalent quantities of the two esters which is kept at 0°, the liquid rapidly thickens, a solid addition product begins to separate, and in 5 to 10 minutes the entire mixture solidifies. It now contains 75 to 80% addition product, and as this does not increase when the mixture is allowed to stand for several hours it evidently represents the amount in equilibrium under these conditions. A small quantity of ammonia, methyl amine, or piperidine may be substituted for the sodium methylate without altering the result. Diluting the mixture with a solvent both diminishes the rate and shifts the equilibrium towards the left, as would be expected, but the latter effect can be counteracted by operating at a lower temperature; in an equal volume of methyl alcohol at -20° the amount of addition product is still 72-75%.

¹⁸ Claisen, Ber., 12, 629 (1879).

At 0° in the presence of these small quantities of base, the reaction does not go beyond the formation of the addition product, or more probably it does not go further at a rate that is significant. In a mixture that was kept at this temperature for 4 hours no unsaturated compound could be detected by the delicate test with permanganate. The isolation of the pure addition product, therefore, involves only its separation from the unchanged esters and the base used as catalyst. This is, however, not at all easy to accomplish. The equilibrium is so mobile that the substance partially reverts to its components when it is dissolved in any solvent in the presence of even the small quantity of base that is occluded by the crystals. In the presence of acids, on the other hand, it slowly loses water and passes into the unsaturated compound. After comparing a number of methods for handling the material we adopted the following procedure.

Four or five drops of a saturated solution of sodium methylate in methyl alcohol is added to a mixture of 16.4 g. of methyl benzoylformate and 13 g. of methyl cyanoacetate. The mixture is shaken in ice water until it has completely solidified (10-15 minutes), then placed in a freezing mixture in which it is allowed to remain for an equal length of time. It is then thoroughly mixed with about 10 cc. of acetyl chloride, care being taken to break up any small lumps that may form in the process, filtered, washedfirst with cooled acetyl chloride diluted with ether, and finally very thoroughly with water—and dried. This leaves about 20 g. of a very finely divided solid that melts at 140-145°, and usually can be recrystallized without further trouble, but occasionally contains traces of occluded base. It is best, therefore, to digest it with 10 cc. of acetyl chloride for several hours, during which the fine powder is changed into small lustrous crystals. The substance is now analytically pure, but still melts poorly at 140-145°. It probably contains a small quantity of a stereoisomer because, while the melting point improves somewhat on repeated recrystallization from ether or chloroform, it becomes sharp at 155° after recrystallization from chloroform that contains a small quantity of phosphorus pentachloride.

Dimethyl α -Phenyl- α -cyano- β -hydroxysuccinate. I.—The addition product is sparingly soluble in ether and acetyl chloride, moderately soluble in chloroform and in carbon tetrachloride, readily soluble in acetone and in methyl alcohol. It crystallizes from chloroform in 6-sided plates, from ether in hard lustrous tables. It does not lose water when heated by itself but even the purest specimens partially dissociate into methyl benzoylformate and methyl cyano-acetate when heated to a high temperature in glass.

Analysis. Calc. for C₁₃H₁₃O₅N: C, 59.3; H, 4.9; N, 5.3. Found: C, 58.9; H, 5.1; N, 5.2.

Dimethyl α -Phenyl- β -cyano-ethylene Dicarboxylate. II.—The unsaturated condensation product is much easier to get and to handle than the addition product. When the mixtures that give the saturated compound at low temperatures are allowed to stand at the ordinary temperature or when the amount of catalyst is increased the principal product is the unsaturated compound. The reaction is reversible but the process is slow and the equilibrium favorable. The most effective condensing agent is sodium methylate, but when this is used as the catalyst there are complications due to the water which is one of the products of the reaction. This not only destroys the methylate but also leads to by-products, because both benzoylformic and cyano-acetic esters are hydrolyzed with uncommon ease. The following experiments illustrate the formation of the substance by direct condensation.

I. A small quantity of a solution of sodium methylate was added to a solution of 5 g. (1 molecular equivalent) of methyl benzoylformate and 4 g. (1.3 molecular equivalents) of methyl cyano-acetate in 10 cc. of dry methyl alcohol. The mixture was boiled for an hour during which alkalinity was maintained by successive additions of small quantities of the alcoholate—in all about 0.2 molecular equivalent. The clear, pale yellow solution was then kept at the ordinary temperature for several days during which it gradually deposited a mass of colorless crystals. These were washed with cold methyl alcohol and recrystallized either from ether or methyl alcohol. The average yield in 5 condensations by this method was 72%.

II. A mixture of 5 g, of the ketonic ester and 4 g, of the cyano ester was diluted with 1 cc. of methyl alcohol and then treated with 0.2 g, of methylamine hydrochloride and 0.2 g, of dry sodium carbonate. After standing at room temperature for 3 days this mixture began to deposit crystals of the unsaturated compound. After 3 weeks the yield of pure unsaturated ester was about 70%.

The ester is also easily obtained by the action of bases or of acids on the hydroxy ester. Thus, when a drop of concd. sodium methylate solution was added to 5 g. of the finely powdered ester suspended in 5 cc. of dry methyl alcohol, the liquid became pale yellow, the hydroxy ester gradually disappeared, and large crystals of the unsaturated compound took their place. After 5 days, during which alkalinity was maintained by occasional additions of methylate, the yield was 75%.

The most satisfactory method for transforming the hydroxy into the unsaturated ester consists in heating its solution in glacial acetic acid. For this purpose a suspension of the ester in 4 times its weight of glacial acetic acid is digested on a steam-bath for 3 hours. It is then free from hydroxy ester. The unsaturated ester may be isolated either by diluting the solution with just enough water to produce a faint milkiness or by pouring it into sodium carbonate solution and extracting with ether. The only by-product in either case is a trace of acid.

Analysis. Calc. for C13H11O4N: C, 63.7; H, 4.5. Found: C, 63.8; H, 4.5.

The ester melts at 79–80°. It is moderately soluble in ether and in cold methyl alcohol, sparingly soluble in benzene, and insoluble in petroleum ether. When allowed to crystallize slowly from methyl alcohol it separates in large, transparent prisms. Its solution in acetone reduces permanganate with great ease.

III. Proof of the Structure of the Condensation Products

Our formula for the addition product is based on the method by which it is obtained and on its relation to the unsaturated ester which is formed from it by the elimination of water. But few substances are known which are constituted like this unsaturated compound. These are

The characteristic property of all of these substances is their extreme resistance to hydrolysis. Our unsaturated compound shows the same peculiarity, but we succeeded in transforming it into two stereoisomeric acids that still contained the cyanogen group. We undertook, therefore, to relate it to phenylfumaric acid but were balked by the behavior of these dibasic acids, when they were heated. One of them readily lost water and formed an anhydride; the other sublimed without decomposition.

$$\begin{array}{c} C_6H_5CCO \\ \parallel \\ CNCCO \\ IV \end{array} \begin{array}{c} C_6H_5CCO_2H \\ \parallel \\ CNCCO_2H \end{array} \begin{array}{c} C_6H_5CCO_2CH_3 \\ \parallel \\ C(CN)CO_2CH_4 \end{array} \begin{array}{c} C_6H_5CCO_2H \\ \parallel \\ C(CN)CO_2CH_5 \end{array} \begin{array}{c} C_6H_5CCO_2H \\ \parallel \\ C(CN)CO_2CH_5 \end{array}$$

The problem was finally solved by the addition of hydrogen to the unsaturated ester as well as to one of the dibasic acids and by transforming the hydrogenated compounds into phenyl succinic acid.

$$\begin{array}{c} C_6H_5CCO_2H \\ \parallel \\ CNCCO_2H \end{array} \longrightarrow \begin{array}{c} C_6H_6CHCO_2H \\ \parallel \\ CNCCO_2H \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCO_2H \\ \parallel \\ CNCHCO_2H \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCO_2H \\ \parallel \\ CH(CO_2H)_2 \end{array} \longrightarrow \begin{array}{c} C_6H_5CHCO_2H \\ \parallel \\ CH_2CO_2H \end{array}$$

Hydrolysis of the Unsaturated Ester with Bases.—Fourteen and four-tenths g. of the ester was added to 100 cc. of a cold saturated solution of potassium hydroxide in methyl alcohol. The ester dissolved at once and a crystalline solid soon began to separate from the solution. After the mixture had been kept at the ordinary temperature for 36 hours, the solid was removed, and thoroughly washed, first with dry methyl alcohol, finally with dry ether. It was completely soluble in water. From its water solution concd. acids precipitated an unsaturated dibasic acid, while dil. acids precipitated the corresponding acid potassium salt.

 α -Cyano- β -phenylmaleic Acid, III.—The acid is precipitated from solutions of its salts in fine very pale yellow needles. It is moderately soluble in warm water; readily soluble in acetone, in alcohol, and in ether; almost insoluble in chloroform, in carbon disulfide, and in petroleum ether. As it does not crystallize well from any of these solvents, it was dried in a vacuum and analyzed without further purification.

Analysis. Calc. for C₁₁H₇O₄N: C, 60.8; H, 3.2. Found: C, 60.7; H, 3.3.

The acid potassium salt, precipitated by adding dil. acid to aqueous solutions of the dipotassium salt, is moderately soluble in water or methyl alcohol. It was recrystallized from the latter, and thus obtained in colorless needles that melted at 193-195°.

Analyses. Calc. for C₁₁H₆O₄NK: K, 15.3. Found: 15.5, 15.3.

α-Cyano-β-phenylmaleic Anhydride, IV.—When the unsaturated dibasic acid is heated rapidly it melts with effervescence at about 142°. The effervescence is due to loss of water, which begins at a much lower temperature, and the melting point is that of the anhydride. The ease with which the acid loses water accounts for the difficulties met in recrystallizing it; solutions in boiling water deposit the anhydride in place of the acid. The substance was recrystallized from ether, from which it separated in fine yellow needles that melted at 145-146°.

Analysis. Calc. for C₁₁H₅O₃N: C, 66.3; H, 2.5. Found: C, 66.3; H, 2.6.

All attempts to hydrolyze either the condensation product or the unsaturated dibasic acid to the corresponding tribasic acid were unsuccessful. Cold alcoholic potassium hydroxide produced no further effect. Concd. aqueous alkalies attacked the cyano ester only on heating; ammonia was given off freely but the alkali evidently reversed the condensation reaction, because the principal product was benzoyl-formic acid.

Hydrolysis of the Unsaturated Ester with Acids.—The cyanogen group in the condensation product is just as resistant to the action of acids as it is to that of bases. The ester was recovered almost completely from a solution in dry methyl alcohol which had been saturated with hydrogen chloride and kept at the ordinary temperature for 3 days; and the result was the same when a similar solution was heated for 27 hours in a steamjacketed autoclave. A partial hydrolysis of the ester was obtained as follows.

A mixture composed of 10 g. of ester, 10 g. of glacial acetic acid, and 20 cc. of coned. sulfuric acid was heated first on a steam-bath for 3 hours, and finally at the boiling point for 5 minutes. It was then cooled and diluted with water whereupon it very slowly deposited 3 g. of pale yellow crystals.

 α -Cyano- β -phenylfumaric Acid, V.—The acid crystallizes from boiling water in colorless plates containing 2 molecules of water of crystallization which is given off below 100°. The anhydrous acid melts without decomposition at 158–160°, and in a vacuum sublimes without change. It is readily soluble in acetone, moderately soluble in methyl alcohol and in boiling water, sparingly soluble in chloroform and in ether.

Analyses. Calc. for $C_{11}H_7O_4.2H_2O$: H_2O , 14.2; C, 52.2; H, 4.4. Found: H_2O , 14.5; C, 52.3; H, 4.4.

This method of hydrolysis was very unsatisfactory; it never gave more than 30% of the possible amount of dibasic acid, in many cases it gave much less or none, and it was always difficult to get a pure product.

Reduction.—The unsaturated dibasic acid was reduced with sodium amalgam, and the ester catalytically in the presence of platinum. In each case a part of the material was reduced further than to the corresponding saturated compound, the reduction involving also the cyanogen group. The product obtained by catalytic reduction was ultimately transformed into phenylsuccinic acid, but as the reduction with sodium amalgam proved to be more satisfactory only this will be described.

Thirty per cent. more than the calculated amount of 2% sodium amalgam was added in the course of 3 hours to an aqueous solution of the dipotassium salt, the alkalinity being reduced from time to time by the addition of acid. The solution was then made feebly acid and shaken with ether. This extracted an acid which after crystallization melted at 168–169°. This substance was also isolated from the mixture by boiling the product from catalytic reduction with alkali.

Analysis. Calc. for C₁₁H₁₃O₄N: C, 59.2; H, 5.8. Found: C, 59.2; H, 6.1.

The substance contains nitrogen, and the composition corresponds to that of the amino acid which would be obtained by complete reduction: C₆H₈CH₂(CO₂H)CH-(CH₂NH₂)CO₂H.

The filtrate from the amino acid was evaporated to complete dryness, the residue first extracted with acetone to remove the last of the amino acid, then dissolved in water and acidified with concd. hydrochloric acid. This precipitated an acid which melted at 162–164°, and gave a methyl ester that melted at 56–57°. It was completely identified by comparison with a specimen of phenylsuccinic acid prepared according to Bredt and Kallen. 14

Trimethyl-phenylethane Tricarboxylate, C6H5CHCO2CH3

-Some of the dipotas-CH(CO₂CH₂)₂

sium salt of the unsaturated ester was reduced with sodium amalgam, which was added rapidly at a low temperature. After half an hour the alkaline solution was decanted from the mercury, acidified with excess of strong hydrochloric acid, and extracted with ether. The ether, on evaporation, left an oil. This was esterified with methyl alcohol and hydrogen chloride. The resulting ester was purified by recrystallization from a mixture of ether and ligroin. It crystallizes in needles and melts at $107-108^{\circ}$.

Analysis. Calc. for C14H16O6: C, 60.0; H, 5.7. Found: C, 59.7; H, 5.6.

IV. Addition of Dimethyl Malonate to Methyl Benzoylformate

The addition was brought about in exactly the same way as that of methyl cyano-acetate. It apparently took place with the same rapidity and resulted in an equilibrium not very different from that formed in the case of the cyano ester, the yield of solid addition product being about 80%. The solid was digested with acetyl chloride and then recrystallized from ether.

Analysis. Calc. for $C_{14}H_{16}O_7$: C, 56.8; H, 5.4. Found: (I) C, 56.5; H, 5.5. (II) C, 56.8; H, 5.4.

Molecular Weight: Calc. for $C_{14}H_{16}O_7$: mol. wt., 296. Found, in freezing glacial acetic acid: 304.

Trimethyl β -Phenyl- β -hydroxy-ethane- α , α , β -tricarboxylate, $C_6H_5C(OH)CO_2CH_3$

CH(CO₂CH₂)₂

The addition product is sparingly soluble in ether, moderately soluble in benzene, chloroform and carbon tetrachloride, readily soluble in acetone and glacial acetic acid. It crystallizes from ether in lustrous prisms and melts at 109–111°. The pure substance is stable, but like the analogous product obtained with cyano-acetic ester it is extremely sensitive to alkalies. This is illustrated by our first attempt to determine its molecular weight by the boiling-point method. The solvent was methyl alcohol which had been distilled from lime and then slowly redistilled twice with the aid of an efficient still head. The substance (2.7547 g.) was added to the boiling solvent (23.43 g.) in pellets. It dissolved at once but the boiling point continued to rise steadily for half an hour. When it finally became constant the elevation (0.48°) corresponded to a molecular weight of 215 instead of 296 calculated. Similar results were obtained in carefully purified acetone. In these cases methyl benzoylformate could be detected by the odor and its presence was definitely established by pouring the solutions into water, extracting with ether and shaking the ethereal solution with bisulfite.

That this reversal of the addition reaction is due to the presence of a trace of base was established as follows. The substance was recrystallized from ether which had been washed with 1:1 sulfuric acid and distilled. The acetone was refluxed with tartaric acid, distilled and fractioned with the aid of a Glinsky still head. Using these materials the

¹⁴ Bredt and Kallen, Ann., 293, 342 (1896).

boiling point became constant in 4 minutes and did not change materially in 3 hours; 2.0713 g. of substance in 23.1 g. of acetone produced an elevation of 0.556° corresponding to a molecular weight of 274 instead of 296 calculated.

Dimethyl β-Phenyl-ethylene-α,α,β-tricarboxylate, C₆H₅CCO₂CH₃

As the un

saturated ester was obtained only as a liquid it was not easy to determine the effect of dehydrating agents on the hydroxy ester. We used, therefore, the means that had been found most effective in the case of the corresponding cyano compound. A solution of the ester in phosphorus oxychloride containing a little more than one equivalent of phosphorus pentachloride was sealed up in a tube and heated in a steam-jacketed autoclave for several hours. The chlorides of phosphorus were then removed with ice water, the oil dissolved in ether, the ethereal solution washed with sodium carbonate, dried and distilled. Under a pressure of 10 mm. most of the product distilled at 180–190°. Thus far the oil has shown no tendency to crystallize.

Analysis. Calc. for C₁₄H₁₆O₆: C, 60.4; H, 5.0. Found: C, 59.8; H, 5.1.

Hydrolysis and Reduction.—A small quantity of the oil was added to cold coned. alcoholic potassium hydroxide. It dissolved at once and a solid potassium salt soon began to separate. This was washed with methyl alcohol and ether, then redissolved in water and acidified. As the resulting acid was a liquid it was neutralized and reduced at 40° with excess of sodium amalgam. The result was a solid acid that melted at 190°. Spiegel¹⁵ gives 191°, Alexander¹⁶ 170–171° as the melting point of phenylethane tricarboxylic acid. On esterification with methyl alcohol it gave a methyl ester that melted at 108° and when it was heated it lost carbon dioxide, forming phenylsuccinic acid which was identified by its melting point and that of a mixture with a sample of this acid.

Summary

- 1. At low temperatures, in concentrated solutions, and in the presence of sodium methylate, ammonia, methyl amine and piperidine, methyl benzoylformate and methyl cyano-acetate react and very quickly form the equilibrium, $C_6H_5COCO_2CH_3$ + $CH_2(CN)CO_2CH_3$ \longrightarrow $C_6H_5-C(OH)CO_2CH_3$
- CH(CN)CO2CH3.
- 2. At higher temperatures, the product of the reaction is an unsaturated ester which can also be formed by eliminating water from the addition product.
- 3. The reaction between methyl benzoylformate and dimethyl malonate is in every respect like that with the cyano-acetate.
- 4. The question whether the unsaturated compounds which are obtained in reactions like these are formed by addition and loss of water from the resulting aldol or ketol, or by some other path, remains to be answered; but it is certain that neither aldol condensation nor the reaction between aldehydes or ketones and substances containing active hydrogen involves the enolization of aldehydes or ketones.

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¹⁵ Spiegel, Ann., 219, 31 (1883).

¹⁶ Alexander, ibid., 258, 76 (1890).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE REACTION BETWEEN CYANO-ACETIC ESTERS AND BENZALACETONE

By E. P. Kohler and Paul Allen, Jr.
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In a paper dealing with the mechanism of the reaction between ethyl cyano-acetate and ketones Haworth¹ used as one of his illustrations the condensation of this ester with benzalacetone. In this reaction he obtained an unsaturated acid for which he gives the melting point 188° and which he represents by Formula I. He hydrolyzed this first to an acid amide, II, and finally to an another monobasic acid melting at 190° to which he ascribes Formula III.

$$\begin{array}{cccc} C_0H_6CH:CHC(CH_3):C(CN)CO_2H, & C_0H_6CH:CHC(CH_3):C(CONH_2)CO_2H \\ & & & I \\ & & & & II \\ & & & & C_0H_6CH:CHC(CH_3):CHCO_2H \end{array}$$

Vorländer,² 12 years earlier, had made a careful study of this same reaction. By almost exactly the same procedure that was used by Haworth, he obtained an unsaturated monobasic acid melting at 180°, which on complete hydrolysis gave another monobasic acid which melted at 187–188°. Vorländer showed pretty conclusively that these substances are the hydroresorcinol derivatives represented by Formulas IV and V.

We have repeated this condensation following Haworth's procedure exactly, and obtained a product melting at 180°. Although there was no reasonable doubt that this is a hydro-resorcinol derivative, we, nevertheless, oxidized it with permanganate. The product was phenylsuccinic acid, which could not possibly be formed from the unsaturated compound represented by I, but would be the normal oxidation product of a substance represented by IV. Vorländer's conclusions are, therefore, confirmed in every respect, and Haworth's products are represented by IV, V and VI. The process by which the hydro-resorcinol derivative is formed may be represented as follows:

¹ Haworth, J. Chem. Soc., 95, 480 (1909).

² Vorländer, Ann., 294, 253 (1897).

The first step constitutes Michael's reaction which, as was shown by Vorländer in the paper cited, is reversible. In the presence of the large amounts of sodium alcoholate used by Vorländer and by Haworth the concentration of the primary addition is always small but when the amount of condensing agent is reduced to a trace there is no difficulty in isolating the intermediate compound. The process is, therefore, exactly like that considered in the preceding paper, the conjugated system behaving, as usual, like an elongated carbonyl group.

Experimental Part

I. Condensation According to Vörlander and to Haworth

A suspension of sodium ethyl cyano-acetate in alcohol was made by adding 28 g. of ethyl cyano-acetate to a concentrated solution of sodium ethylate containing 5 g. of sodium. To this was added a solution of 36 g. of benzalacetone in just enough alcohol to liquefy it. When this mixture was heated it turned dark and gradually deposited a solid sodium compound. After this had been heated for an hour it was removed, washed thoroughly with absolute alcohol and ether until it became nearly white, dissolved in water, and acidified. The resulting solid, after repeated recrystallization from methyl alcohol, melted constantly at 180°; yield, 26.5%. Three more condensations carried out with variations in the conditions gave the same product.

Methyl Ether.—Dry hydrogen chloride was passed slowly into a methyl alcoholic solution of the condensation product for 15 minutes. The solution on evaporation deposited a solid which had the composition of a methyl ether, melted at 171–172°, and in every way answered Vorländer's description of the methyl ether of cyanophenyl-dihydro-resorcinol. There can, therefore, be no doubt that Haworth's product is identical with that previously obtained by Vorländer.

Oxidation.—A solution of 9.4 g. of the condensation product melting at 180–181° in sodium carbonate was treated with aqueous permanganate until the color no longer disappeared at the ordinary temperature; this required 33.5 g. All the organic products were collected in ether by suitable operations, and the acids were then extracted from the ether with sodium carbonate. From the carbonate solution hydrochloric acid precipitated a solid which melted at 165° and which gave a methyl ester that crystallized in tables and melted at 58°. The melting points of phenylsuccinic acid and of its methyl ester are given as 168° and 57°, respectively. As the observed melting points are slightly different from these, the ester was analyzed.

Analysis. Calc. for C12H14O4: C, 64.8; H, 6.2. Found: C, 64.5; H, 6.4.

These results prove that the oxidation product is phenylsuccinic acid and that Vorländer's formula for the condensation product is right.

II. Condensation with a Small Quantity of Sodium Methylate Methyl α -Cyano- β -phenyl- γ -acetyl Butyrate, $C_0H_5CHCH_2COCH_3$

HC(CN)CO₂CH₃.—

A 5% solution of sodium methylate was added drop by drop to a solution of 27.5 g. each of benzalacetone and methyl cyano-acetate until the mixture was alkaline to litmus. The solution was then boiled for about 12 hours, alkalinity being maintained meanwhile by addition of small quantities of the methylate solution as required. The resulting yellow liquid was freed from alcohol by distillation and from acids by solution in ether and extraction with sodium carbonate. The ether on evaporation left an oil. As this showed no tendency to crystallize, it was rectified under diminished pressure. The fractions collected below 190° contained unchanged ketone which was identified by its melting point and probably also unchanged cyano ester. The very pale yellow liquid distilling at about 196° at 7 mm. was analyzed; yield, 32.5 g., or 70.2%.

Analyses. Calc. for $C_{14}H_{16}O_3N$: C, 68.6; H, 6.2. Found: C, 68.7, 68.6; H, 6.2, 6.2. The Ethyl Ester.—In the hope that the ethyl ester might solidify, ethyl cyano-acetate was substituted for the methyl ester in the condensation with benzalacetone; but it likewise was obtained only as a very viscous oil. It boils at 203° at 12 mm. The yield was 50%.

Analysis. Calc. for C₁₅H₁₇O₂N: C, 69.5; H, 6.5. Found: C, 69.2; H, 6.6.

Semicarbazone.—As all efforts to induce the esters to solidify were fruitless, the methyl ester was converted into a semicarbazone in order to get a solid compound for identification. To this end a strong solution containing semicarbazine and a large excess of potassium acetate was made by adding a saturated methyl alcoholic solution of potassium acetate to a concentrated solution of 4 g. of the hydrochloride in water, and removing the precipitated potassium chloride. The clear solution obtained in this way was mixed with a solution of 3 g. of the addition product in methyl alcohol and the mixture set aside. It soon began to deposit the semicarbazone in minute white needles that melted at 156–157°.

Analysis. Calc. for C15H18O3N4: C, 59.6; H, 6.0. Found: C, 59.3; H, 6.2.

Internal Condensation.—A concentrated methyl alcoholic solution of the methyl ester was boiled with the equivalent quantity of sodium methylate for an hour. The sodium salt which separated was washed with alcohol and ether, then dissolved in water. From the water solution acids precipitated cyano-phenyl-dihydro-resorcinol which melted at 181°.

Dimethyl β -Phenyl- γ -acetyl-ethylmalonate, $C_{\delta}H_{\delta}CHCH_{2}COCH_{3}$

CH(CO₂CH₃)₂.—

A solution of 3.5 g. of the cyano ester in methyl alcohol was saturated with hydrogen chloride and set aside. On slow evaporation it deposited a

colorless solid which after recrystallization from methyl alcohol melted at 64°. The filtrate, on suitable treatment, yielded more of the same substance, the total yield being about 60%. It is much more easily obtained by direct addition of dimethyl malonate to benzalacetone. Thus a methyl alcoholic solution containing 2.4 g. of ketone and 3 g. of ester was allowed to stand at room temperature for several days during which it was kept alkaline by successive additions of a few drops of a dilute solution of sodium methylate. On evaporation it deposited a pale yellow solid, which became colorless on recrystallization. When the substance was heated alone or mixed with the product from the cyano ester the melting point was 64°.

Analysis. Calc. for C₁₅H₁₈O₅: C, 64.7; H, 6.5. Found: C, 64.4; H, 6.3.

The substance has neither the composition nor the properties of a dihydro-resorcinol derivative. As it does not reduce permanganate it cannot be an unsaturated compound such as would be formed by addition to the carbonyl group of the ketone. It must, therefore, have the structure assigned to it.

Summary

- 1. In the presence of a small quantity of sodium alcoholate, benzalacetone combines with cyano-acetic esters and malonic esters. The products are saturated compounds formed by addition to the double linkage of the ketone.
- 2. In more concentrated solutions of the alcoholate the addition products undergo further condensation to hydro-resorcinol derivatives. The reaction, therefore, takes place in the manner stated by Vorländer, and Haworth's interpretation is incorrect.

Cambridge 38, Massachusetts

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

ASYMMETRIC DYES

By C. W. PORTER AND HARRY K. IHRIG Received June 11, 1923

During the past 5 years, 35 asymmetric dyes have been synthesized in this Laboratory and studied with reference to the possibility of selective dyeing. We have held the opinion that selective absorption of an optically active form from a racemic mixture by silk, wool or living tissue would constitute evidence of chemical, rather than physical, union between the dye and the substance which it colors. Interest in this type of investigation has been stimulated by the observation that optically active forms of other types of asymmetric compounds show specific biochemical reactions.¹

¹ Neuberg and Wohlgemuth, Ber., 34, 1745 (1901). Piutti, Compt. rend., 103, 134 (1886). Mayor, Ber., 37, 1225 (1904).

Willstätter recognized the importance of finding out whether the asymmetric molecules of protein-like substances such as silk and wool would accomplish the resolution of a racemic dye by combining with one form only, but at that time there were no asymmetric dyes in existence.²

Porter and Hirst³ prepared several asymmetric dyes by treating p-aminobenzophenone with Grignard reagents, diazotizing the condensation products, and coupling with various amines and phenols. They reported the selective absorption by wool of the levo form of one of their dyes. They were unable to obtain reproducible results of a quantitative character.

Ingersoll and Adams have prepared optically active derivatives of d- and l-phenylamino-acetic acid and obtained evidence of selective absorption of one of them by wool.⁴

The work reported in this paper represents a successful attempt to accomplish the resolution of a racemic dye by the selective action of wool.

Two new series of asymmetric dyes were produced. The members of the first group were made by producing asymmetric amines through the condensation of bromo acid bromides with acetanilide, then diazotizing these products and coupling with various aromatic amines and naphthols. The dyes of the second series were prepared from amino-mandelic acid by diazotizing the acid and coupling with aromatic amines and with naphthols.

Optically active compounds were obtained by resolving racemic aminomandelic acid into its d and l forms before diazotization. The resolution was accomplished by fractional crystallization of the cinchonine salts. Dyes derived from d- and l-m-mandelic acid and β -naphthol melt at 210° and have specific rotations of $+47^{\circ}$. \pm .5° and -47° . \pm .5°.

When wool is dyed in a racemic mixture of these dyes, the solution containing the unused portion of the compound is levorotatory. Both forms of the dye are taken up by the wool but they are absorbed at different rates. By using an excess of wool and extending the time of contact to 72 hours the residual dye in solution was almost a pure levorotatory compound.

Experimental Part

m-Nitromandelic Acid.—m-Nitrobenzaldehyde was made by the action of chromyl chloride and water on a solution of m-nitrotoluene in carbon disulfide.⁵ The aldehyde was treated with potassium cyanide and acetic acid. The resulting cyanohydrin was hydrolyzed by Heller's method.⁶ The reduction of the nitro compound to aminomandelic acid was accomplished by means of ferrous sulfate and barium hydroxide. A solution of 20 g. of m-nitromandelic acid in 200 cc. of warm water was treated with a suspension of 255 g. of crystallized barium hydroxide in 1200 cc. of water, and a solution of 184 g. of crystallized ferrous sulfate in 800 cc. of water. The suspension of barium hydroxide was obtained by heating the water until all of the base had dissolved, then cooling the solution and constantly shaking it. The reduction proceeded rapidly at 30°,

² Willstätter, Ber., 37, 3758 (1904).

Porter and Hirst, This Journal, 41, 1264 (1919).

⁴ Ingersoll and Adams, ibid., 44, 2930 (1922).

⁵ Widmann, Ber., 13, 678 (1880).

⁶ Heller, ibid., 46, 280 (1913).

the whole mass changing in color from green to brown within a few minutes. After the mixture had been vigorously stirred for an hour, it was filtered. The clear filtrate was treated with sulfuric acid until all of the barium had been precipitated and the solution was distinctly acid. The barium sulfate was removed by filtration and the filtrate evaporated on a water-bath. The product was recrystallized from hot water. The crystals melt with decomposition at 130° . The yield was about 60° .

Resolution of m-Amino-mandelic Acid.—A suspension of 20 g. of crystalline cinchonine and 11 g, of m-aminomandelic acid in 500 cc. of water was heated on the waterbath for an hour, and shaken frequently. After cooling, the solution was filtered and allowed to stand in an open vessel at room temperature. The first crystals appeared after 4 days. Later, however, seeding decreased the time to a few hours. The crystals were roset-shaped and on drying fell to a powder. They were recrystallized from hot water (25 cc. of water for each g. of the dry salt); m. p., 156.5°. The pure crystals were dissolved again in hot water and the solution was cooled to room temperature, treated with ammonium hydroxide until all the cinchonine was precipitated and the solution gave the odor of ammonia. The cinchonine was filtered off and the filtrate was freed from ammonia by evaporation at room temperature over sulfuric acid in a vacuum desiccator. It was then acidified with hydrochloric acid and the evaporation was continued at room temperature. The dextrorotatory amino acid crystallized in a few days. It was recrystallized twice from water; m. p. 130° (decomp.); $[\alpha]_p = +33.80^\circ$. After several crops of mixed crystals had been removed from the mother liquor the levo product was obtained nearly pure by fractional recrystallization at ordinary temperatures. The yield was poor; m. p., 130° (decomp.); $[\alpha]_{\rm p} = -33.65^{\circ}$.

Dextro-m-Azo-β-naphthol-mandelic Acid.—d-m-Aminomandelic acid prepared as described above was diazotized at 0° and poured into a cold alkaline solution of β-naphthol. The solution became blood red. The dye was precipitated by making the solution faintly acid, and was recrystallized from glacial acetic acid. It is soluble in bases, slightly soluble in alcohol and in acetic acid, insoluble in water; m. p., 210° ; $[\alpha]_D = +49^{\circ} \pm 5^{\circ}$

Levo-m-Azo- β -naphthol-mandelic Acid.—This dye was prepared by the methods applied in the synthesis of the dextro compound. Its color, melting point, solubility and other properties are identical with the corresponding properties of the dextrorotatory dye; $[\alpha]_D = -49^{\circ} \pm 5^{\circ}$.

Dyeing Experiments

Many experiments were made with fresh, clean wool and with silk. The fibers were dyed by pure d and pure l derivatives of m-mandelic acid and β -naphthol, and by racemic mixtures of the dyes. The rates of absorption have not been measured, but a typical example, indicating selective absorption, may be given. A solution containing 1 g. of the racemic dye in 75 cc. of acetic acid was treated with 2.5 g. of wool at 20° for 24 hours. The solution was then filtered and its rotation measured. A 250watt nitrogen-filled Mazda lamp was used as a source of light. (This dye gives an optically clear solution, and satisfactory readings of the colored solution can be made.) At the end of 24 hours the reading was -0.66°. Fresh wool was then added. At 48 hours the reading was -0.91°. Control samples of wool in acetic acid without the dye did not develop optical activity. There was no extraction of optically active compounds from the wool.

Other Compounds.—Incidentally, in the course of this investigation, the following compounds, not mentioned above, were prepared and analyzed.

p-Azo-β-naphthol-mandelic Acid, HO·C₁₀H₆·N:N·C₆H₄·CHOH·COOH.—From diazotized p-aminomandelic acid and β-naphthol; it is a bright red dye, insoluble in acids but soluble in bases and in hot alcohol; m. p., 118°. Calc.: N₂, 8.7. Found: 8.45, 8.23.

p-Azo-resorcinol-mandelic Acid, $(HO)_2C_6H_4\cdot N: N\cdot C_6H_4\cdot CHOH\cdot COOH.$ —A red dye, soluble in bases, slightly soluble in alcohol and in acetic acid; m. p., 154° (decomp.). Calc.: N_2 , 9.72. Found: 10.95, 11.14.

p-Azo-dimethylaniline-mandelic Acid, $(CH_3)_2N\cdot C_6H_4\cdot N:N\cdot C_6H_4\cdot CHOH\cdot COOH.$ —A brown dye, insoluble in bases but soluble in acids and slightly soluble in water. It becomes bright red in acid solution; m. p., $125-129^\circ$ (decomp.). Calc.: N_2 , 14.05. Found: 14.21, 13.95.

m-Azo-resorcinol-mandelic Acid, (HO)₂C₆H₃·N:N·C₆H₄.CHOH·COOH.—A red dye, soluble in alcohol, water and in bases; m. p., over 280° .

m-Azo-dimethylaniline-mandelic Acid, $(CH_3)_2N \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot CHOH \cdot COOH.$ —A reddish-purple dye, soluble in acids and in alcohol but insol. in bases; m. p., 158°.

m-Azo-phenol-mandelic Acid, $HO \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot CHOH \cdot COOH$.—A bright yellow compound, soluble in bases and in hot alcohol, but insoluble in acids; m. p., 119°. Calc.: N_2 , 10.33. Found: 10.56.

β-Naphthol-azo-α-hydroxy-propionophenone, CH_3 ·CHOH·CO· C_0H_4 ·N: N· $C_{10}H_7H$.— A red dye made by condensing α-bromopropionyl bromide with acetanilide, hydrolyzing the condensation product, diazotizing the resulting p-aminopropionophenone and coupling with β-naphthol. It is soluble in alcohol, ether and bases, and insoluble in water and in acids; m. p., 132°. Calc.: N_2 , 9.00. Found: 9.39, 9.34, 9.37.

β-Naphthol-azo-α-hydroxybutyrophenone, CH₃·CH₂·CHOH·CO·C₆H₄·N:N·C₁₀-H₇OH.—A red dye from p-aminobutyrophenone and β-naphthol. It is soluble in bases, alcohol, or acetone and insoluble in acids; m. p., 72°.

 β -Naphthol-azo- α -hydroxy-isovalerophenone, (CH₂)₂CH·CHOH·CO·C₆H₄·N:N-C₁₀H₇OH.—A red dye from the condensation product of α -bromo-isovaleryl bromide and acetanilide by hydrolysis, diazotization of the amine and coupling with β -naphthol. It is soluble in benzene, ether or bases and is insoluble in acids; m. p., above 265°.

Summary

Representatives of 2 series of asymmetric dyes have been prepared, analyzed and described.

A dye derived from m-aminomandelic acid and β -naphthol has been obtained in pure optically active forms.

The dextro form of this dye combines with wool faster than does the corresponding levo form.

BERKELEY, CALIFORNIA

[Contribution from the Chemical Laboratory of the University of North Carolina]

DIRECT CONVERSION OF DERIVATIVES OF DICHLORO-ACETIC ACID INTO DERIVATIVES OF TRICHLORO-ACETIC ACID

By Alvin S. Wheeler and Samuel C. Smith¹ Received June 14, 1923

In a paper just published by us² it was shown that nitrodichloro-acetanilides are formed when the isomeric nitro-anilines are treated with dichloro-acetic acid in the presence of phosphorus pentoxide. During the progress of this study it was observed that the reaction between o-toluidine and dichloro-acetic acid took a different course when no dehydrating agent was present. When the substances are brought together at 0° or below in the molecular ratio of 1:1, a simple salt of o-toluidine and dichloro-acetic acid is formed, analogous to aniline acetate. On the other hand, when an excess of acid is used and the heat of the reaction is allowed to take its course, a complex reaction takes place, the product being a trichloro-acetic acid derivative which appears to be a salt of o-toluidine and trichloro-acetic acid. We then turned our attention to other amines and found the same to be true of aniline, p-toluidine, q-naphthylamine and q-nitro-aniline.

Very little study has been made of the reaction between dichloro-acetic acid and aromatic amines. Beamer and Clarke³ state that they prepared aniline dichloro-acetate, melting at 122° , and aniline trichloro-acetate melting at 140° , but do not substantiate their claims by any analyses; hence their work is of little significance. Our aniline trichloro-acetate melts at 163° , and not at 140° . Baralis⁴ describes a p-toluidine dichloro-acetate, m. p. 140– 141° and a p-toluidine trichloro-acetate, m. p. 137° . We prepared the latter compound and find that it melts at 135° . The journal containing this article is not in the Chemical Abstract list and we have so far been unable to locate it in any library.

A number of articles have been published which describe reactions of dichloro-acetic acid and aromatic amines yielding products containing no chlorine, such as those of Meyer,⁵ Duisburg⁶ and Heller.⁷

The production of trichloro-acetic acid derivatives from dichloro-acetic acid proceeded so smoothly that we felt it necessary to examine the purity

- ¹ This paper constitutes a portion of Part II of a thesis by Samuel C. Smith submitted in candidacy for the degree of Doctor of Philosophy in June, 1923, at the University of North Carolina.
 - ² Wheeler and Smith, This Journal, 45, 1839 (1923).
 - ³ Beamer and Clarke, Ber., 12, 1066 (1879).
 - 4 Baralis, Rev. chim. med. farm., 2, 301.
 - ⁵ Meyer, Ber., 16, 925 (1883).
 - ⁶ Duisburg, ibid., 18, 190 (1885).
 - ⁷ Heller, Ann., 332, 253 (1904).

of our dichloro-acetic acid. It was redistilled and the portion boiling at 191° was used in our work

Calc. for C₂H₂O₂Cl₂ (mol. wt., 129): Cl, 55.03. Found: 55.09.

The further precaution was taken of treating the same amines with trichloro-acetic acid. The compounds were identical in every case with those made from dichloro-acetic acid. Again, the composition of the trichloro compounds was proved by regenerating the constituents. For example, aniline trichloro-acetate obtained from dichloro-acetic acid was decomposed by sodium hydroxide, aniline being set free, whereas treatment of an alcoholic solution with sulfuric acid gave the ethyl ester of trichloroacetic acid. The identity of the latter was proved by its conversion into trichloro-acetamide; m. p., 141°.

A complete analysis was made in one case only, that of o-toluidine trichloro-acetate made from dichloro-acetic acid.

The constitution of the compounds may be represented by one of the following formulas.

rmulas. O
$$H_3$$
 OH H I $CCl_3-C-O-N-C_6H_5$ or II $CCl_3-C-N-C_8H_5$

In I we have a pentad nitrogen and therefore an ammonium salt. In II we have a triad nitrogen and a compound of the chloral hydrate type, in which 2 hydroxyl groups are attached to one carbon atom, the stability of such a compound being due to the strong negative environment of the 3 chlorine atoms. The decomposition products which we have obtained throw no light on whether one is better than the other, but we lean to Formula II.

In order to explain why we get a trichloro and not a dichloro compound, we must conceive that 2 molecules of dichloro-acetic acid are rearranged into 1 of trichloro-acetic acid and one of monochloro-acetic acid under the influence of the amine which is basic in character: 2 CClClHCOOH → CCl₃.COOH + CH₂ClCOOH.

It may seem inconsistent to employ an outside agent (phosphorus pentoxide) in any of these reactions in view of the basis on which this study is built, but it was found important to do so in order to facilitate the identification of monochloro-acetic acid in the same reaction with trichloro-acetic acid. The last compounds described in the experimental part are the nitroacetanilides of these acids.

Experimental Part

Dichloroacetates

o-Toluidine Dichloro-acetate, CH₃C₆H₄NH₂.CHCl₂COOH.—A solution of 5 g. of o-toluidine in 20 cc. of carbon tetrachloride was slowly mixed with a solution of 6.1 g. of dichloro-acetic acid in a like amount of the solvent while kept cold with ice. A dense

precipitate formed which weighed 8.5 g. It crystallized out of alcohol in prismatic crystals; m. p., 140°. The salt is pure white but turns brown on exposure to the air and light. Continued boiling with water converts it into o-toluidine trichloro-acetate.

Analysis. Subs., 0.2496: AgCl, 0.3078. Calc. for $C_9H_{11}O_2NCl_2$ (mol. wt., 236): Cl, 30.08. Found: 30.51.

p-Toluidine Dichloro-acetate, CH₂C₆H₄NH₂.CHCl₂COOH.—This compound was prepared in the same way as the o-toluidine salt. If care is not taken to hold the temperature down, the reaction takes a different course and a mixture of products is obtained, as shown by its low melting point. This may explain the low melting point, 140°, found by Baralis; our product melts at 160°. Recrystallized from alcohol, the crystals are prismatic and pure white, but turn brown on exposure to the air.

Analysis. Subs., 0.5401: AgCl, 0.6665. Calc. for $C_9H_{11}O_2NCl_2$ (mol. wt. 236): Cl. 30.08. Found: 30.55.

Trichloro-acetates

Aniline Trichloro-acetate, (from Dichloro-acetic Acid), $C_6H_6NH_2.CCl_3.COOH.$ —To 5.0 g. of aniline was added 7 cc. of dichloro-acetic acid. A great deal of heat was evolved as the product crystallized. Water was added and heat applied until the product dissolved. As the solution cooled, a mass of colorless crystals formed which melted at 160°. Several recrystallizations from water raised the melting point to 163°; yield of crude product, 7.5 g.

Analysis. Subs., 0.2440: AgCl, 0.4088. Calc. for C₈H₈O₂NCl₃ (mol, wt. 256.5): Cl, 41.52. Found: 41.44.

The substance crystallizes from hot water in colorless plates that turn reddish on exposure to the air. It is very soluble in hot water, slightly so in cold water, soluble in alcohol, slightly soluble in ether or benzene. It is decomposed by potassium hydroxide solution, and aniline is set free, as proved by the melting point (198°) of its hydrochloride. It is also decomposed by sulfuric acid. In this case trichloro-acetic acid was proved to be a product by its conversion into ethyl trichloro-acetate, boiling at 170° (756 mm.) and the formation of the trichloro-acetamide from this ester; m. p., 141°.

Aniline Trichloro-acetate (from Trichloro-acetic Acid).—To 5.0 g. of aniline was added 9.0 g. of trichloro-acetic acid. When the mixture was heated gently a vigorous reaction took place. The product crystallized from hot water in plates that melted at 163°. The constituents were also brought together in carbon tetrachloride solution at —3°. The same product, melting at 163°, was obtained. Beamer and Clarke⁸ give 145° as the melting point, but they made no analysis.

Analysis. Subs., 0.4878: AgCl, 0.8149. Calc. for $C_8H_8O_2NCl_3$ (mol. wt., 256.5): Cl, 41.52. Found: 41.10.

This product is therefore identical with the one obtained from dichloro-acetic acid. o-Toluidine Trichloro-acetate (from Dichloro-acetic Acid), CH₃C₆H₂NH₂CCl₃CO-OH.—Five g. of o-toludine and 7 cc. of dichloro-acetic acid were mixed. The reaction proceeded as described above. The product crystallized from hot water in colorless plates; m. p., 167-168° (decomp.).

Analyses. Calc. for $C_0H_{10}O_2NCl_3$ (mol. wt., 270.5): C, 39.92; H, 3.69; N, 5.17; Cl, 39.37. Found: C, 40.04; H, 3.70; N, 5.11; Cl, 38.93.

o-Toluidine trichloro-acetate decomposes at its melting point, two products being identified as chloroform and carbon dioxide. It is slightly soluble in cold water, very soluble in hot water, soluble in acetone, alcohol, insoluble in benzene or ligroin. Potassium hydroxide liberates o-toluidine, shown by the melting point of its hydrochloride,

⁸ Ref. 3, p. 1067.

214-216°. Sulfuric acid liberates trichloro-acetic acid, shown by converting it into its ethyl ester and its amide.

o-Toluidine Trichloro-acetate (from Trichloro-acetic Acid).—Five g. of o-toluidine and 8.0 g. of trichloro-acetic acid were heated together. The product was recrystallized from hot water and proved to be identical with the compound described above in melting point (167–168°), crystal form and solubility.

Analysis. Subs., 0.5122: AgCl, 0.8147. Calc. for $C_9H_{10}O_2NCl_3$ (mol. wt. 270.5): Cl, 39.37. Found: 39.34.

p-Toluidine Trichloro-acetate (from Dichloro-acetic Acid), CH₃C₆H₄NH₂.CCl₃COOH.—Five g. of p-toluidine was added to 7 cc. of dichloro-acetic acid. Much heat developed and to the mixture while still hot was added 20 cc. of water. A light yellow precipitate formed. This was recrystallized from hot water except for a small insoluble portion. The pure substance consists of colorless prismatic needles; m. p., 135° (decomp.). The solubilities correspond to those of the ortho compound.

Analysis. Subs., 0.3385: AgCl, 0.5353. Cale. for $C_9H_{10}O_2NCl_3$ (mol. wt., 270.5): Cl, 39.37. Found: 39.11.

p-Toluidine Trichloro-acetate (from Trichloro-acetic Acid).—Five g. of p-toluidine was mixed with 8.0 g. of trichloro-acetic acid. The product crystallized from hot water in prismatic needles; m. p., 135° (decomp.).

Analysis. Subs., 0.5021: AgCl, 0.7978. Calc. for $C_9H_{10}O_2NCl_3$ (mol. wt., 270.5): Cl, 39.37. Found: 39.31.

 α -Naphthylamine Trichloro-acetate (from Dichloro-acetic Acid), $C_{10}H_7NH_2.CCl_3CO-OH$.—Five g. of α -naphthylamine was mixed with 9.1 g. of dichloro-acetic acid and the mixture warmed a little, since the reaction in this case was somewhat slow. No solution was apparent. The mush of crystals was washed with 50 cc. of water. The crude product, melting at 170°, weighed 10.4 g., the calculated amount being 10.7. After the substance was washed with boiling water or recrystallized from dilute alcohol the melting point was raised to 173°, with decomposition. The compound crystallizes from alcohol in pale violet plates which are only slightly soluble in hot water, are soluble in alcohol or acetone, and insoluble in ether or benzene.

Analysis. Subs., 0.3587: AgCl, 0.4950. Calc. for $C_{12}H_5O_2NCl_3$ (mol. wt., 306): Cl, 34.74. Found: 34.37.

 α -Naphthylamine trichloro-acetate was also made from trichloro-acetic acid by gently heating a mixture of the constituents. Recrystallization from dil. alcohol gave pale violet plates; m. p., 173°.

m-Nitro-aniline Trichloro-acetate (from Dichloro-acetic Acid), $C_0H_4NO_2NH_2.C-Cl_3COOH.$ —To 5.0 g. of m-nitro-aniline was added 15 cc. of dichloro-acetic acid which was sufficient to dissolve it. After the solution had been heated on the water-bath for 10 minutes it was poured into 100 cc. of cold water. The crystalline precipitate formed melted at 143°. Recrystallization from hot water raised the melting point to 147° but continued boiling with water caused hydrolysis. The crystals are pale yellow plates, soluble in alcohol, slightly soluble in ether and insoluble in benzene.

Analysis. Subs., 0.4049: AgCl, 0.5722. Calc. for $C_8H_7O_4N_2Cl_3$ (mol. wt., 301): Cl, 35.32. Found: 34.89.

p-Nitrochloro-acetanilide (from Dichloro-acetic Acid), C₆H₄NO₂NHCOCH₂Cl.— Five g. of p-nitro-aniline was warmed with 12 cc. of dichloro-acetic acid. After reaction had taken place (analogous to the reactions described above), 5.0 g. of phosphorus pentoxide was added and the mixture heated on the steam-bath for 10 minutes, then poured into 100 cc. of cold water and allowed to stand overnight for complete crystallization to take place. The precipitate was then extracted with carbon tetrachloride. The insoluble portion proved to be p-nitrochloro-acetanilide and the solution contained p-nitro-trichloro-acetanilide.

The portion insoluble in carbon tetrachloride was recrystallized from alcohol. It consisted of yellow prisms, m. p. 177° , insoluble in water, soluble in acetone or ether.

Analysis. Subs., 0.3311: AgCl, 0.2191. Calc. for $C_8H_7O_3N_2Cl$ (mol. wt., 214.5): Cl, 16.55. Found: 16.37.

That this compound was p-nitrochloro-acetanilide was proved by comparison with the product made directly from monochloro-acetic acid. To $5.0\,\mathrm{g}$. of p-nitro-aniline was added $5.0\,\mathrm{g}$. of phosphorus pentoxide and $5.0\,\mathrm{g}$. of monochloro-acetic acid. After the mixture had been heated until fusion took place, $100\,\mathrm{cc}$. of water was added. The precipitate formed was recrystallized from alcohol, as yellow prisms; m. p., 177° .

Analysis. Subs., 0.1974: AgCl, 0.1344. Calc. for $C_8H_7O_9N_2Cl$: Cl, 16.55. Found: 16.37.

p-Nitrotrichloro-acetanilide (from Dichloro-acetic Acid), $C_6H_4NO_2NHCOCl_3$.— The portion soluble in carbon tetrachloride was purified by evaporation of the solvent and extraction of the residue with 50% alcohol. The portion insoluble in the alcohol melted at 135-140°. It was recrystallized from carbon tetrachloride. The pure substance consists of light yellow prismatic needles that melt at 140° with previous softening. It is soluble in acetone, alcohol, benzene or chloroform.

Analysis. Subs., 0.0341: AgCl, 0.0521. Calc. for $C_8H_6O_3N_2Cl_3$ (mol. wt., 283.5): Cl, 37.56. Found: 37.79.

To prove that this was p-nitrotrichloro-acetanilide the substance was synthesized from trichloro-acetic acid. To 5.0 g. of p-nitro-aniline was added 5.0 g. of phosphorus pentoxide and 7.0 g. of trichloro-acetic acid. The mixture was heated until it melted. To remove any unchanged p-nitro-aniline dil. hydrochloric acid was used for precipitation. The substance was purified by recrystallizing from carbon tetrachloride and obtained as light yellow needles; m. p., 140°, with previous softening.

Analysis. Subs., 0.2365: AgCl, 0.3598. Calc. for $C_8H_5O_3N_2Cl_3$: Cl, 37.56. Found: 37.61.

Summary

- 1. The dichloro-acetates of o- and p-toluidine were prepared from dichloro-acetic acid.
- 2. The trichloro-acetates of aniline, o- and p-toluidine, α -naphthylamine and m-nitro-aniline were prepared from dichloro-acetic acid. The same trichloro-acetates were prepared from trichloro-acetic acid.
- 3. To prove the presence of monochloro-acetic and trichloro-acetic acids in the reaction of dichloro-acetic acid on aromatic amines, the *p*-nitrochloro-acetanilides were prepared, separated and identified.
- 4. Two molecules of dichloro-acetic acid exchange a hydrogen and a chlorine atom under the influence of these weak bases, thus yielding trichloro-acetic acid derivatives from dichloro-acetic acid.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

THE BROMINATION OF 2-AMINO-PARA-XYLENE AND CERTAIN NEW AZO DYES

By Alvin S. Wheeler and E. W. Constable¹ Received June 16, 1923

E. Fischer and Windhaus² prepared a bromine derivative of 2-amino-pxylene by brominating its formyl derivative. The product contained 1 bromine atom and as for the constitution of the compound they merely say, "The location of the bromine, for which three possibilities exist, is still not known, but we hold it as probable that the halogen is in the position para to the amino (2) group." We have established the location of the bromine definitely at Position 5 by a short series of reactions. Instead of using the formyl derivative of Fischer and Windhaus, we prepared the acetyl derivative and treated this with bromine in glacial acetic acid solution. The monobromo compound thus obtained was hydrolyzed with strong hydrobromic acid, giving the hydrobromide of 2-aminobromo-bxylene, melting at 255°. The free amino acid was identical with the one prepared by Fischer and Windhaus. Its diazotization by the Sandmever method gave 2,5-dibromo-p-xylene, m. p. 75.5°, a compound of known constitution. While this was sufficient to locate the bromine at Position 5. we extended the proof by oxidizing this compound with fuming nitric acid to 2,5-dibromoterephthalic acid, m. p. 316°, and finally converting this into its diethyl ester which melts at 125°.

Having established the constitution of the compound as 2-amino-5-bromo-p-xylene, we prepared a few azo dyes. It was found that the bis compound was produced when the bromo derivative was coupled with phenol, resorcinol and α -naphthol, but not in the case of β -naphthol. The β -naphthol derivative is very brilliant in color, a scarlet-red and the crystals are splendid, long needles. The other dyes are quite ordinary in appearance. Owing to difficulty in making sodium salts, the tinctorial properties on silk and wool were tried by employing the development method of application.

Experimental Part

2-Aceto-amido-5-bromo-p-xylene, (CH₃)₂C₆H₂NHCOCHBr₃.—Five g. of 2-aceto-amido-p-xylene (m. p., 137°) was dissolved in 20 cc. of glacial acetic acid by gentle heating and then cooled. The solution was kept cold while 1 molecular equivalent (4.9 g.) of bromine was slowly added. Five volumes of water were added to the thick mush of crystals that formed and the mixture was well stirred. The yield was equal to the weight

¹ This paper constitutes a portion of a thesis submitted by E. W. Constable in candidacy for the degree of Master of Science in June, 1923, at the University of North Carolina

² Fischer and Windhaus, Ber., 33, 1974 (1900).

of the raw material taken. The crude product melted at 185°, recrystallization from alcohol raising the melting point to 187°. It crystallizes in colorless needles grouped in fluffy masses of rosets, and is very difficultly soluble in water, but soluble in alcohol and in ether. One g. dissolves in 8 cc. of hot alcohol.

Analysis. Subs., 0.2180; AgBr, 0.1639. Calc. for C₁₀H₁₂ONBr (242); Br, 33.05. Found: 33.08.

This compound was prepared by C. K. Brooks in this Laboratory.

2-Amino-5-bromo-p-xylene Hydrobromide, $(CH_3)_2C_6H_2BrNH_2.HBr$.—Five g. of the aceto-amido compound was heated with 75 ec. of hydrobromic acid, d., 1.3. Hydrolysis was completed in a short time, the hydrobromide crystallizing out as the solution cooled. The product weighed 20% more than the raw material. It was recrystallized from absolute alcohol or, better, hydrobromic acid. It consists of flat needles; m. p., 255°, (decomp.).

Analyses. Subs., 0.2059, 0.4346. Calc. for C₈H₁₀NBr.HBr: NaOH, 0.0293, 0.0618. Found: 0.0294, 0.0615.

- **2,5-Dibromo-**p-**xylene**, $(CH_3)_2C_6H_2Br_2$.—The hydrobromide described above was dissolved in water containing some hydrobromic acid and diazotized at a low temperature. After the addition of copper powder and potassium bromide, the mixture was distilled with steam. The crystals that appeared in the distillate were recrystallized from dil. alcohol, water being added to the alcoholic solution until crystallization began. The product consisted of plates; m. p., 75.5° . It was, therefore, identical with the 2,5-dibromo-p-xylene described by Jannasch.
- 2,5-Dibromoterephthalic Acid, $(COOH)_2C_6H_2Br_2$.—The dibromoxylene was heated above 300° with 20 parts of nitric acid, d., 1.15, in a sealed tube for 8 hours. The product consisted of leaf-like crystals that melted at 313° (uncorr.). Fileti and Crosa⁴ give 316–317° as the melting point of 2,5-dibromoterephthalic acid.
- 2,5-Dibromo-diethylterephthalate, (COOC₂H₅)₂C₆H₂Br₂.—The acid was readily esterified by boiling it with absolute alcohol containing a little dry hydrogen chloride. The glistening leaf-like crystals that appeared as the solution cooled melted at 125°. Fileti and Crosa⁵ state that this ester melts at 125°.

Azo Dyes

2,4–(Bis-5-bromo-2-p-xylylazo)phenol, $[(CH_3)_2C_6H_2BrN_2]_2C_6H_3OH$.—One molecular equivalent of aminobromoxylene hydrobromide was diazotized and then treated with $^1/_2$ molecular equivalent of phenol dissolved in a minimum quantity of dil. alkali. After 10 minutes the solution was acidified with acetic acid. The dull brown precipitate that formed was recrystallized from glacial acetic acid. The pure compound consists of small, dark brown scales with a metallic luster when viewed in the mass, while under the microscope they are pale green; m. p., 233–234°. By employing the development method of application this dye may be made to color silk an écru and wool an orange-brown.

Analysis. Subs., 0.1029: AgBr, 0.0759. Calc. for $C_{22}H_{20}ON_4Br_2$ (516): Br, 30.98. Found: 31.39.

2,4-(Bis-5-bromo-2-p-xylylazo)resorcinol, $[(CH_3)_2C_5H_2BrN_2]_2C_5H_2(OH)_2$.—One molecular equivalent of the hydrobromide was diazotized and then treated with $^1/_2$ molecular equivalent of an alkaline solution of resorcinol. After 10 minutes acetic acid was added in excess, producing a dark brown precipitate. This was boiled with ben-

³ Jannasch, Ber., 10, 1357 (1877).

⁴ Fileti and Crosa, Gazz. chim. ital., 18, 309 (1888).

⁵ Ref. 4, p. 310.

zene and the solution filtered hot. From the filtrate the product crystallized in fine, microscopic crystals of claret-brown color in the mass. It was further purified by recrystallizing from a 1:1 mixture of benzene and acetone. The pure substance melts at 263°. By employing the development method of application the dye may be made to color silk an écru and wool a Brazil-red.

Analysis. Subs., 0.0205: AgBr, 0.0146. Calc. for C₂₂H₂₀O₂N₄Br₂ (532): Br, 30.08. Found: 30.01.

2,4-(Bis-5-bromo-2-p-xylylazo) α -naphthol, $[(CH_3)_2C_6H_2BrN_2]_2C_{10}H_5OH$.—This dye was prepared in the same way as were those described above. The product was purified by boiling it in a large quantity of alcohol, filtering the solution while hot and allowing the filtrate to cool. The crystals separating from the cold solution are of indefinite shape, very dark brown to black when viewed in the mass and melt at 222–223°. When applied by the development method, this dye colors silk a Mars-orange and wool a claret-brown.

Analysis. Subs., 0.0325: AgBr, 0.0216. Calc. for $C_{28}H_{22}ON_4Br_2$ (566): Br, 28.23. Found: 28.28.

1-(5-Bromo-2-p-xylylazo) β -naphthol, (CH₃)₂C₅H₂BrN₂C₁₀H₅OH.—One molecular equivalent of the hydrobromide was diazotized, made alkaline and treated with 1 molecular equivalent of β -naphthol in alkaline solution. Acidification produced a brilliant red precipitate, weighing 40% more than the hydrobromide taken. On recrystallizing from acetone it was obtained in very beautiful, long scarlet-red needles in felted masses. Applied as the other dyes above, this dye colors silk a light red and wool a Nopal-red.

Analysis. Subs., 0.0673: AgBr, 0.0360. Calc. for $C_{18}H_{15}ON_2Br$ (355): Br, 22.51. Found: 22.76.

Summary

- 1. Bromination of 2-aceto-amido-p-xylene yields a monobromo derivative in which the bromine is located at Position 5 as proved by the following series of reactions: 2-aceto-amido-bromo-p-xylene (new) \longrightarrow 2-amino-bromo-p-xylene \longrightarrow 2,5-dibromo-terephthalic acid \longrightarrow 2,5-dibromo-diethylterephthalate.
- 2. The following new azo dyes were prepared: 2,4-(bis-5-bromo-2-p-xylylazo)phenol; 2,4-(bis-5-bromo-2-p-xylylazo) α -naphthol; 1-(5-bromo-2-p-xylylazo) β -naphthol.

CHAPEL HILL, NORTH CAROLINA

NEW BOOKS

Beiträge zur Geschichte der Naturwissenschaften und der Technik. (Contributions to the History of Science and Technology.) By Prof. Dr. Edmund O. von Lippmann, Dr. Ing. E. H. at the Technischen Hochschule at Dresden, Director of the "Zuckerraffinerie Halle" at Halle A.S. 314 pp. 2 figs. Verlag von Julius Springer, 1923, Berlin. 16.5 cm. × 24.5 cm. \$1.60 paper, \$1.90 bound.

This last work by Professor Lippmann comprises a selection of miscellaneous papers upon the history of alchemy, chemistry and chemical technology which have been published during the past 10 years in the Chemiker Zeitung, Zeitschrift für Angewandte Chemie and other periodicals.

It was at the request of the numerous friends of his two previous volumes of "Essays and Addresses" (Abhandlungen und Vorträge) upon historical chemistry that the author has compiled this third collection of scattered articles.

The 36 contributions of the new volume show the same variety of interest and scholarly attention to detail that have always characterized the historical researches of Professor Lippmann. "Chemical Papyri of the Third Century" (2 papers), "Origin of the name Caput Mortuum," "First Occurrence of the Word Chemistry," "On the History of Alcohol and Distillation" (6 papers), "Use of Petroleum in the Middle Ages," "Chemical and Technological Contents of the Medieval Receipt Books of Heraklius, Theophilus Presbyter, and Vitalis de Furno" (3 papers), "Chemical and Technological References in Dante," "Petrarch upon Alchemy," "The Alchemists J. I. and I. Hollandus" (2 papers), "The Philosopher's Stone and Homunculus, Two Alchemistic Problems in Goethe's Faust," "A biographical Note upon Liebig," and "The Centenary of Robert Mayer" are selected from the various titles to show the diversity of subjects which are discussed.

As belonging to the author's special field of technology, the papers upon "The Medieval Sugar Industry" and "Sugar Monopolies of the Middle Ages" form important addenda to his well-known "History of Sugar" published in 1890. There are also comments upon several recently discovered letters of Achard (the first manufacturer of beet sugar), a paper upon "Goethe and Sugar Manufacture," an article upon "The History of the Vacuum Pan," and an address upon "The Development of the Sugar Industry in Germany between 1888 and 1913."

For the casual reader of historical chemistry we know of no recent work which provides more pleasant entertainment than this new volume of Professor Lippmann's collected papers; while for those more critically inclined the numerous explanatory footnotes and bibliographic references offer abundant opportunities for additional study.

The book is printed in clear Roman type and is provided with a good index of both names and subjects. It should find a place in the library of every chemist, whether teacher or technologist, who is interested in the cultural aspects of his science.

C. A. BROWNE

Catalytic Action. By K. George Falk, Harriman Research Laboratory, The Roosevelt Hospital, New York. The Chemical Catalog Company, Inc., 1 Madison Avenue, New York, U. S. A., 1922. 172 pp. 23.5 × 15.5 cm. Price \$2.50.

The enormous growth of so-called catalytic industrial operations during the present century has stimulated research in the field of the mechanism of catalysis and indeed of chemical action in general. Owing to the wide range of literature which investigators have to cover it is both important and necessary that from time to time a serious attempt should be made by someone actively interested in the subject to summarize the work in at least its more important aspects. In this respect the monograph of Dr. K. G. Falk is doubly welcome in that it not only fills one of these gaps but it also presents the case in a very readable form with ample references.

The volume contains 8 chapters, the first 3 dealing with the phenomena, criteria and theories of catalytic action. Two chapters are devoted to a discussion of the energy relations and recent theories in chemical action, 2 to enzyme action and life processes, while the last chapter includes a discussion on contact catalysis.

Dr. Falk believes that the only tenable theory of catalytic action is the associative theory which was originally definitely advanced by H. E. Armstrong, and the argument in the whole volume is thrown onto this hypothesis. It is now generally admitted even by the protagonists of the radiation theory that when a catalyst G operates in the union of two substances A and B, a complex of the general type AC or BC is first formed, which then reacts to form the complex ABC, with subsequent decomposition. The stability of these intermediate compounds is also a criterion of the catalytic efficiency of C. The objection to the theory is that it is too vague, since it is in reality merely a restatement of the fact that chemical action is action by contact. We require to know the nature of the complex and why it is more reactive than the original substances in order to obtain some insight into the modus operandi of chemical action and to assist us in the choice of a catalyst that will permit a chemical action to proceed at a determined speed. The author gives an excellent resumé of Stieglitz's work on the hydrolytic decomposition of the imido esters in which definite proof is advanced that the positive ion formed by the complex imido ester H+ is much more reactive than the imido ester atom. It is possible that the transformation of a substance into a charged ion by reaction with either hydrogen or hydroxyl ion may generally increase its reactivity with ions of the opposite sign. An extension of this hypothesis would indicate that an ester would form a complex with either hydrogen or hydroxyl ions and thus serve as the nucleus of an amphoteric electrolyte, a point which might possibly be confirmed by migration experiments. There are, however, many other ways in which molecular reactivity may be produced.

That on association of the catalyst and reactant a molecular rearrangement may take place to give a decrease of free energy of the system is evidenced by citation of the work of Stieglitz and Derick but to include coupled and induced reactions, such as Traube's slow oxidations, in the same category would necessitate a somewhat wide extension of our present ideas on the subject. A study of the oxidation potentials of systems which can be transformed from a coupled to a catalytic reaction by alteration of

the hydrogen-ion concentration of the medium indicates an alternative method of investigation.

The author gives a brief but descriptive review of the various proposed atom structures before dealing with the varied problem of radiation and chemical change, in which the views of the various rivals are expressed impartially; the somewhat important criticisms and suggestions of Lindemann might have been included.

The chapters on enzyme action and life processes are extremely illuminating and present the interesting properties of such colloidal catalysts in a very readable form.

In the chapter on contact analysis the transition of the views of Bodenstein and Fink into the monomolecular film theory of Langmuir is given and a few examples of the varied types of decomposition that may be obtained with different catalysts. It might have been well to have extended the section on promoter action in catalysis, as this may in all probability provide an important method for investigation into two factors influencing surface action, namely, the effect of adsorption of reactants and products and the possible variation in the orientation and polarity of the adsorbed substance with the catalytic material.

Dr. Falk is to be congratulated on the production of an excellent monograph, which is both pleasantly and clearly printed.

ERIC K. RIDEAL

The Formation of Colloids. By The Svedberg, Professor of Physical Chemistry in the University of Upsala. Monographs on the Physics and Chemistry of Colloids. D. Van Nostrand Company, 25 Park Place, New York, 1921. viii + 119 pp. 22 figs. 12.5 × 19 cm. Price \$2.00 net.

This is the first of a series of monographs that The Svedberg proposes to issue. It is his plan to keep the series up to date by new editions of such parts of the subject as develop with special rapidity.

As the author announces in the first monograph, he aims "to give a survey of the processes which cause the formation of colloids—or of heterogeneous systems with a relatively large boundary surface—especially with regard to the conditions that determine the degree of subdivision of the systems formed."

The formation of disperse systems in a vacuum, in gases, in liquids and in solids is presented in a scholarly manner. The discussion of formation in a vacuum is short but extremely interesting. As might be expected, the Bredig process of electric pulverization of metals with the oscillatory arc is discussed ably and at some length. The author favors the view that the sol is formed by condensation of metal gas and the sediment by dispersion of melted metal.

His distinction between volume condensation and surface condensation (p. 57) is interesting. In this connection he cites the striking fact that ul-

traviolet light converts an alcoholic solution of sulfur into a colloidal suspension by transforming the sulfur into another allotropic modification.

Among the best features of the monograph are the pages devoted to colloidal gold with their detailed equations and the excellent historical discussion of this particular colloid. Good, also, is the treatment of sulfur.

Peptization deserves fuller treatment. We find on p. 108 that "the so-called peptization processes are in general to be considered as reversible coagulations. They are not real dispersion processes, the degree of dispersion not being altered by the peptization, but only the mutual distances of the particles." The difference between peptization by solvent and by solute is not stressed. Under "Dispersion" the preparation of emulsions was merely touched upon but doubtless this will later become the subject of a complete monograph. The Plauson mill and the Premier mill are either too recent in development or too uncertain to be mentioned.

Colloid chemistry will be debtor to Svedberg for this series of monographs. He writes with authority.

HARRY N. HOLMES

Organic Syntheses. Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. II. James Bryant Conant, Harvard University, Editor-in-Chief; Roger Adams; Hans Thacher Clarke; Oliver Kamm. John Wiley and Sons, Inc., New York; Chapman and Hall, Limited, London, 1922. vii + 100 pp. 3 figs. 23.5 × 15 cm. Price \$1.50.

The first volume of the "Organic Syntheses" was favorably reviewed in detail by E. P. Kohler.¹ The second volume now at hand reaffirms in the preface the purpose of this series: "The preparation of materials for research, always time-consuming and annoying, is made increasingly so by the inexactness of the published information which so often omits essential details. Because of this, much needless experimentation is necessary in order to obtain the results given in the published reports. As the additional information thus acquired is seldom published, duplication of such experiments occurs again and again,—a waste of time and material. It is hoped these difficulties may be remedied by the publication of this series of pamphlets. In other words, the authors hope to make this a clearing house for the exchange of information as to methods of preparation of some of the most needed organic chemical reagents."

As is well known, we owe to the Department of Chemistry of the University of Illinois the inception of the laudable purpose expressed in the above quotation. Four pamphlets under the title "Organic Chemical Reagents," edited by Roger Adams and co-workers, have been published by that University. The present new series of Organic Syntheses "aims to make available in a permanent form complete detailed directions for the preparation of various organic chemical reagents." In fact, nine out

¹ This Journal, 43, 2702 (1921).

of the twenty-five preparations in Vol. II, of the "Organic Syntheses" are reproduced from the "Organic Chemical Reagents, II" with only slight changes.

The reliable nature of the laboratory directions for the various substances is vouched for by several investigators, and the names of the chemists who have studied the experiments is attached to each preparation, "so that further information concerning any obscure point can be obtained if any question arises in using these directions." The order of treatment is: (1) Procedure,—giving explicit directions for the preparation of the substance in 250g. to 2kg. lots; (2) Notes,—which explain why it is essential to observe the conditions laid down in the directions; (3) other methods of preparation, including a complete bibliography on the particular substance.

The preparation of the following organic chemicals is included in this volume: benzalacetophenone; benzyl benzoate; benzyl cyanide; α, γ -dichloro-acetone; p-dimethylamino-benzaldehyde; ethyl oxalate; ethyl phenylacetate; glycerol α, γ -dichlorohydrin; glycerol α -monochlorohydrin; hydrazine sulfate; mesitylene; methyl red; p-nitrobenzoic acid; p-nitrobenzyl cyanide; p-nitrophenylacetic acid; nitroso-p-naphthol; phenylacetic acid; phenylacetylene; phenylhydrazine; phthalimide; quinoline; quinone; sodium p-toluenesulfinate; 1,3,5-trinitrobenzene; 2,4,6-trinitrobenzoic acid.

The editors deserve the hearty support, as well as the thanks of the chemical profession. Let us hope that the issue of Vol. III will not be long delayed.

M. GOMBERG

Qualitative Organic Analysis. By OLIVER KAMM. 260 pp. John Wiley and Sons, Inc., New York, 1923. 15 × 23 cm. Price \$1.75.

This laboratory textbook is essentially the course in Qualitative Organic Analysis that has been given to his classes at the University of Illinois by Professor Kamm. A careful examination of its contents has convinced the reviewer that when used under a competent instructor it should prove an admirable and practical one. As the author remarks in his preface: "Qualitative Organic Analysis has not been taught generally because of the assumption on the part of the chemists that the multiplicity of organic compounds excludes the possibility of a systematic procedure. This is the opinion only of those who have not taught the subject; those who have had experience in presenting the work both in the classroom and laboratory realize that qualitative organic analysis is capable of logical and systematic treatment and that it is of fundamental importance in the training of the chemist in the organic field."

The work is specially arranged for a one semester course of 32 laboratory periods of 3 hours each, the first week being given to solubility tests

of known compounds, 5 weeks to the classification of known compounds, 6 weeks to the identification of 6 or 8 individual compounds, and 4 weeks to the examination of mixtures. The section of classified tables of compounds at the end of the book enables the student to apply the knowledge gained to a great diversity of substances, and the training in fundamental principles and methods given is so varied and well planned that the work as a whole deserves the highest commendation.

Special emphasis is rightly given to the importance of the solubility of different classes of organic compounds for purposes of classification, separation and identification. Due attention is, however, also given to special methods for the determination of the chemical class to which a compound belongs by application of chemical tests to the small scale preparation of characteristic derivatives, to the determination of physical constants, and to the special technique of small scale preparations.

The book deserves a hearty welcome wherever organic chemistry is taught.

S. P. MULLIKEN

The Chemistry of Urea. The Theory of its Constitution, and of the Origin and Mode of its Formation in Living Organisms. By EMIL A. WERNER, Sc.D., Professor of Applied Chemistry in the University of Dublin. Longmans, Green and Company, 55 Fifth Avenue, New York; 39 Paternoster Row, London, E. C. 4; Toronto; Bombay, Calcutta and Madras; 1923. xii + 212 pp. 24.5 × 15.5 cm. Price \$4.75 net.

This volume is one of a series of monographs on biochemistry edited by R. H. A. Plimmer and F. G. Hopkins. The chemistry of urea is a subject of quite general interest and, hence, contributions to our knowledge of it will, indeed, be welcomed by many investigators.

The subjects listed in the table of contents of this monograph include the following: history of urea, mechanism of Wöhler's synthesis, constitution of cyanic acid, thermal decomposition of urea, decomposition of urea when heated in presence of acids and alkalies, interaction of urea and nitrous acid, mechanism of syntheses of urea from derivatives of carbonic acid, miscellaneous syntheses of urea, synthesis of urea from cyanamide, conditions necessary for the existence of true carbamides, properties of urea on the basis of the cyclic formula, occurrence of urea in nature, constitution of salts of ammonia and their relation to urea, and decomposition of urea in alkaline solution by hypochlorites and hypobromites.

The body of the material is presented in 15 chapters, the logical sequence of which is to be commended. A summary of methods for the detection and estimation of urea is presented in Appendix I. Appendix II gives the physicochemical constants of urea and also contains a short discussion of urea formation in its relation to nitrogen fixation. An extensive bibliography is appended which, though by no means complete, should be of assistance to those interested in this subject.

The material is presented from a much more restricted point of view than the title of the book and the chapter headings indicate, being limited essentially to a polemical discussion of the constitution of urea. As stated by the author in the preface, one of the main objects of the book is to refute the long-standing conception of the carbamide formula for urea, and to show that the cyclic formula proposed by himself disposes of disagreements between facts and theory in the chemistry of urea. The choice of material presented has been rather closely governed by this object and it is somewhat unfortunate that the fact is not more accurately reflected in the title of the work. The limited treatment of the subject is further indicated in the preface by the statement "the chemistry of substituted derivatives of urea is outside the scope of this work which is restricted to the consideration of the constitution of urea itself."

Since it is not the function of a single reviewer to pass upon the merits of the arguments which the author leaves to the judgment of all who are interested, it would be somewhat out of place to enter here into any detailed discussion. The book appears to be an excellent presentation of the views of the author but the reviewer believes that critical readers will fail to be convinced by the arguments offered in many instances. For example, those investigators who have had experience with the behavior of cyanamide in aqueous acid or alkaline solutions will certainly fail to agree with the author's impressions as set forth in Chapter IX, concerning the constitution of cyanamide, the mechanism of its polymerization and its relation to urea. The deductions as to the constitution of urea drawn from its relation to cyanamide are based on entirely erroneous information.

In the discussion of the subject "Urea and Nitrogen Fixation" the statement, "The fact that cyanamide is not directly hydrolyzed to urea, but requires a concentration of acid necessary to produce a salt of urea appears to be a serious drawback to the economic production of urea from this source," is likewise in error.

The book has a cardboard binding and the quality of the paper is rather poor, but the presswork is very good.

I. M. BRAHAM

The Journal of the American Chemical Society

with which has been incorporated The American Chemical Journal (Founded by Ira Remsen)

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[CONTRIBUTION FROM GOLDSMITHS' METALLURGICAL RESEARCH LABORATORY, CAMBRIDGE UNIVERSITY]

THE ATOMIC WEIGHT OF ANTIMONY FROM DIFFERENT SOURCES. I. PRELIMINARY

By Sheikh D. Muzaffar Received January 11, 1923

Ever since the discovery of isotopes, investigation of samples of an element from different sources has become important. Values for the density, the melting point and the atomic weight may show slight variations among different samples. The differences are accounted for on the isotopic theory, and whenever observed indicate the presence of isotopes in an element.

A review of the earlier work on the atomic weight of antimony suggested that its equivalent weight might be different in samples prepared from ores from different parts of the earth. With this idea in mind the present work was undertaken with stibnites from Hungary, Bolivia, Borneo and Peru. The results indicate a striking variation in the value of the atomic weight, but since this seems to be the second case of its kind (that of lead being the first), the figures need a confirmation by the study of the element from other sources and by more work on the methods of the purification of the element. This is, therefore, a preliminary notice of the phenomenon.

Preparation of Materials

Ammonium Bromide was prepared according to the method suggested by A. Scott.¹ Silver.—Through the kindness of Mr. C. T. Heycock, a sample of silver was used that had been purified and employed by him in his work on the atomic weight of rubidium, and also by A. Scott¹ in his work on the ratio of ammonium bromide to silver.

Arsenious Oxide, a chemically pure grade, was sublimed 6 times at 90° in a long, evacuated hard-glass tube which was sealed under reduced pressure and warmed before sealing to fill it with the vapor of the substance. The oxide was weighed into the titration bottles immediately after its preparation.

¹ Scott, J. Chem. Soc., 103, 849 (1913).

Potassium Bromate, a chemically pure grade purchased from a commercial source, was found to contain 0.02% of hygroscopic moisture when it was dried in a vacuum desicator over fused calcium chloride. Accessory Reagents used in the analytical work, or incidental to the purification of materials, were purified and always tested to assure their freedom from interfering impurities. Distilled water was specially prepared and was free from ammonia.

Preparation of Pure Antimony

Stibnites from Peru, Bolivia, Borneo and Hungary were obtained. Each ore was separately digested in concd. hydrochloric acid and from the extract antimony trichloride was obtained by fractional distillation at 220° followed by 5 redistillations. The chloride was next transformed into chloro-antimonic acid (SbCl₅.HCl.4¹/₂H₂O) by the method of W. Schmid.² SbCl₃ + Cl₂ + $4^{1}/_{2}$ H₂O \longrightarrow SbCl₅.HCl. $4^{1}/_{2}$ H₂O. The fourth crop of the crystals of this salt was broken up in a large amount of distilled water and the solution boiled to complete the hydrolysis. Antimonic acid thus precipitated was washed and evaporated to dryness with nitric acid to expel the last traces of the chloride. The antimony oxide thus formed was reduced with potassium cyanide in silica crucibles and the metal cast in plaster moulds free from iron. The buttons of antimony obtained were scrubbed with clean sand and from them a 1mm, layer was filed off all around. They were then washed thoroughly and etched in dil. sulfuric acid, washed again in distilled water and melted in silica crucibles under borax. The metal was kept at its melting point for a long time and slowly cooled. It was again superficially cleaned as described above, and powdered in an agate mortar.

The powdered metal was melted in a current of pure dry hydrogen over a lime support as employed by T. W. Richards in his purification of silver. Bright buttons of antimony thus obtained were etched, dried and powdered in an agate mortar. The powdered metal was heated in a current of pure dry hydrogen to dry it and to reduce the traces of oxide that may have been formed during powdering. This treatment was given just before the metal was weighed for the determination of the density or the atomic weight.

All of the 4 samples of antimony were prepared and purified under identical conditions to assure their superficial uniformity. The method as outlined above was suggested by E. Groschuff⁴ after a rigorous investigation and comparison of all the methods so far known for obtaining pure antimony, and was adopted by H. H. Willard and McAlpine⁵ in the preparation of antimony for determination of its atomic weight.

Balance and Weighings.—Weighings were made on a balance sensitive to 0.05 mg., using standardized weights and the method of substitution.

- ² Schmid, Z. anorg. Chem., 44, 37 (1905).
- ³ Richards, This Journal, 27, 459 (1905).
- 4 Groschuff, Z. anorg. Chem., 193, 164 (1918).
- 5 Willard and McAlpine, This Journal, 43, 797 (1921).

Ratio of Potassium Bromate to Arsenious Oxide

Method.—Arsenious acid was transferred directly from the balance pan into stoppered bottles. After a few cubic centimeters of sodium hydroxide solution had been added, the bottles were warmed on a waterbath to effect solution, and when they had cooled 100 cc. of moderately strong hydrochloric acid was poured into each. Titration with potassium bromate solution was carried out in exactly the same manner as described later for antimony.

On standardization, 1.000 g. of potassium bromate in solution was found to be equivalent to 0.0034487 g. of arsenious oxide. The ratio $3As_4O_6$: $4KBrO_3$ was found to be: (1) 1.78154, (2) 1.77983, (3) 1.77870, (4) 1.77455, (5) 1.77805, (6) 1.77901, (7) 1.77875; av., 1.778633. The calculated molecular weight of potassium bromate is 167.02; that determined from the above ratio is 166.92, with 0.02% moisture and 0.04% experimental error.

Ratio of Ammonium Bromide to Silver

This was determined in a Stas box by the method of A. Scott.¹ Ammonium bromide solution was standardized against silver. 1.000 g. was found to be equivalent to 0.00108015 g. of silver or 0.00098082 g. of silver bromide. One g. of silver nitrate solution was equivalent to 0.99335 g. of ammonium bromide solution. Solid ammonium bromide was compared to pure silver and the ratio NH₄Br: Ag was found to be (1) 0.90770, (2) 0.90734, (3) 0.90788; av., 0.90776. From this the atomic weight of silver is determined to be 107.91. This is affected by 0.03% experimental error.

Ratio of Silver to Potassium Bromate

A weighed quantity of potassium bromate was transferred to a stoppered bottle, dissolved in distilled water and reduced to potassium bromide with a slight excess of sulfur dioxide solution. The bottle was then warmed and a few drops of fuming nitric acid were added to oxidize sulfite to sulfate. In a separate bottle the requisite quantity of silver was dissolved in nitric acid according to the method of Stas. Both the bottles were taken into a dark room, and the silver solution after dilution was transferred completely into the bromide solution bottle. The titration was completed in the Stas box in the same manner as described for the ratio of ammonium bromide to silver. The ratio KBrO₃: Ag was found to be (1) 1.54923, (2) 1.54875, (3) 1.54900, (4) 1.54900, (5) 1.54892; av., 1.54924 (reduced to a vacuum). The molecular weight of potassium bromate, from the ratio, is found to be 167.13, from which 0.02% moisture and 0.045% experimental error are to be deducted.

Ratio of Antimony to Potassium Bromate

Antimony was dried in a current of hydrogen immediately before use. It was weighed by transfer from a weighing bottle into a clean, conical flask. The metal was dissolved in concd. sulfuric acid and the cooled

solution was transferred completely to a stoppered bottle containing 100 cc. of distilled water and 20 cc. of hydrochloric acid. A quantity of potassium bromate, approximately but slightly less than equivalent, was weighed, dissolved in hot distilled water and the solution poured into the bottle that contained antimony solution, in small quantities at a time. The reaction is represented by the equation 3SbCl₃ + KBrO₃ + 6HCl → 3SbCl₅ + KBr + 3H₂O. Since the quantity of potassium bromate added is less than the equivalent amount, an excess of antimony trichloride is left in the above process. This was titrated with 0.01 N potassium bromate solution, using methyl orange as the indicator. The bromate solution was standardized against the sample of antimony under consideration. As the ratio of the metal to bromate is different with different samples of antimony, the standardization of the solution was repeated before each new sample of the metal was analyzed. The solution was drawn from a weight pipet and the strength expressed as grams of antimony equivalent to 1.000 g. of solution. The amount of antimony that reacted with the solution was deducted from the total antimony taken, and thus only that quantity of the metal was considered that had reacted with the solid bromate. All of the samples of antimony were titrated under precisely the same conditions; therefore, there could be no error of experiment that could modify the relative differences of the element from different sources. The ratio of the different samples of antimony to potassium bromate. 3Sb: KBrO₃, was found to be as follows.

Table I

Ratio of the Various Samples of Antimony to Potassium Bromate

KAHO OF THE VARI	OUS SAMPLES OF	ANTIMONY TO LOTAS	STUM DRUMATE
	Sam	ples from	
Hungary	Borneo	Peru	Bolivia
2.17590	2.1828	2.1857	2.2001
2.17593	2.1830	2.1863	2.2001
2.17590	2.1802	2.1869	2.1970
2.17589	2.1875	2.1865	2.1986
2.17594	2.1857	2.1863	2.1998
2.17595	2.1846	2.1859	2.1975
2.17593	2.1811	2.1860	2.1986
	After repurifica	tion of the same sam	ple 2.1990
			2.1982
			2,1979
			2.1985
	Atomic	Weights	
121.144	121.563	121 720	122 374

In conclusion the author wishes to express his thanks to Mr. C. T. Heycock for his keen interest in the problem.

Summary

Antimony metal has been prepared from stibnites from Hungary, Borneo, Peru and Bolivia, and compared with potassium bromate by

solution in sulfuric acid, addition of solid potassium bromate and completion of the titration with $0.01\ N$ potassium bromate solution. The purity of potassium bromate was established by comparison with silver and arsenious acid. The atomic weights of antimony thus obtained are as follows: stibnite from Hungary, 121.14; from Borneo, 121.56; from Peru, 121.72; from Bolivia, 122.37.

CAMBRIDGE, ENGLAND

[CONTRIBUTION FROM THE LABORATORY OF GRINNELL COLLEGE]

ELECTROMETRIC TITRATION OF IODATE, BROMATE, CHLORATE, FERRICYANIDE WITH TITANOUS SULFATE

By W. S. HENDRIXSON Received May 22, 1923

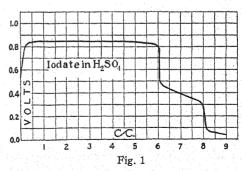
In a recent paper from this Laboratory¹ it was stated that work was in progress on the titration of oxidizing substances with titanous ion.

In the work described in the present paper the same general methods and the same apparatus as mentioned in the former paper were used. The stirrer was provided with a mercury seal and all titrations were carried out in an atmosphere of carbon dioxide. All solutions affected by light were kept in bottles coated with a black enamel paint, provided with siphons and never unstoppered. Titanium solutions were standardized with permanganate and dichromate. The latter and the solutions of pure potassium iodate, bromate and chlorate were made up by weight and the contents of calibrated flasks at 20° .

Titration of Iodate with Titanous Ion

A 0.05 N solution of iodate was made up by weight and also standardized with pure iodide and thiosulfate. The volume of the solution at the end

of the titrations was about 300 cc. and its acidity was between N and 2 N with sulfuric acid. Hydrochloric acid was unsatisfactory. A sharp drop of about 0.3 volt occurred when the iodate was all decomposed, as shown in Fig. 1. The iodine set free reacted slowly on further addition of titanium and an excess was required to drive the



reaction to completion. Possibly the sharp rise in voltage at first shows the effect of hypo-iodous acid, the first fall the decomposition of all the iodate, and the final fall the completed reduction of the iodine. The

¹ Hendrixson and Verbeck, This Journal, 44, 2382 (1922).

second fall is fairly sharp but irregularly delayed by about 1 cc., the average for the determinations of Table I being 29.92 cc., while that calculated is 28.95. The correct end-point is found by multiplying the volume of titanium at the first fall by 1.2, which is in accord with the following equations representing the stages in the reduction:

$$5\text{Ti}_2(SO_4)_3 + 2\text{HIO}_3 + 5\text{H}_2SO_4 = 10\text{Ti}(SO_4)_2 + 6\text{H}_2O + \text{I}_2$$
 (1)
 $\text{Ti}_2(SO_4)_3 + \text{I}_2 + \text{H}_2SO_4 = 2\text{Ti}(SO_4)_2 + 2\text{HI}$ (2)

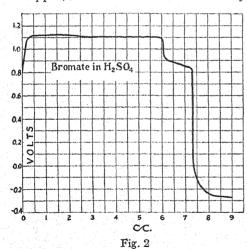
Table I gives the results thus obtained. The concentration of the titanous solution was $0.05~N~\times~1.727$; 50 cc. of iodate solution was used in each experiment.

TABLE I
TITRATION WITH TITANOUS ION

$Ti_2(SO_4)_3$, ec	24.05	24.05	24.20	24.12	24.10
Iodate factor	0.997	0.997	1.003	1,000	0.999
			A·	v., 0.05 N	× 0.999

Titration of Bromate with Titanous Ion

After the first draft of this paper had been written there came to the notice of the author the work of Zintl and Wattenberg, in which they used bromate as one of the substances for back-titration in the determination of copper,² and of arsenic and antimony with titanium.^{2b} In their first



paper the work was carried out at 80° and no adequate description is given of the details of the titration of bromate against titanium. Their work does not seem to interfere with the main purposes of this study, which have been to ascertain whether these halogen acids could be accurately and quickly determined directly and at room temperature with titanous salts, and by the electrometric method.

Pure potassium bromate free from bromide, iron and other impurities likely to occur, was

used in making a $0.05\ N$ solution. In the first series, the titration vessel containing 50 cc. of bromate solution, 200 cc. of boiled water and 10 cc. of $10\ N$ sulfuric acid, was filled with carbon dioxide after which the vessel³ was closed air-tight except for the exit through the mercury seal. The

² Zintl and Wattenberg, (a) Ber., 55, 3366 (1922); (b) 56, 472 (1923).

³ Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," 1918, p. 65.

curve obtained on adding titanium in excess strikingly resembles that for iodate and is shown in Fig. 2. The sudden rise at first and the two falls in potential have the same meaning. Apparently either fall may be used for determining the end-point, by calculation, of course, if the earlier fall is used. In this work the long, abrupt fall marking the disappearance of the bromine was preferred. In some experiments free way was provided for the escape of bromine from the titration vessel and its passage over potassium iodide solution, but only a trace of free iodine was obtained. When the vessel was tightly stoppered, therefore, the escape of bromine must have been negligible.

Five experiments carried out as described gave the concentration of the bromate solution $0.05~N~\times~1.002$, with the average deviations from this factor +0.0007 and -0.004.

Hydrochloric acid can be used to advantage instead of sulfuric, if not in concentration sufficient to set bromine free before the titration vessel can be filled with carbon dioxide. Apparently, it should not greatly exceed 0.5 N at the end of the titration. In the presence of this acid a smaller amount of bromine seems to be set free, the two reactions running more or less simultaneously, and the end-point is more quickly reached. The first fall in potential, found when sulfuric acid is used, is nearly obliterated in the presence of hydrochloric. In Table II the acid varied from 0.5 N to N, and the concentration of the titanium solution was 0.05 $N \times 1.4663$; 50 cc. of bromate solution was used in each experiment.

TABLE II

Titration of Bromate with Titanous Ion in Hydrochloric Acid 50 cc. of Bromate Solution Used

The literature shows increasing use of bromate as an analytical reagent, making greater the need of methods for its rapid and accurate determination under various conditions. It is hoped to give this matter further and more detailed study.

Titration of Chlorate with Titanous Ion

Knecht and Hibbert³ and Kikuchi⁴ have titrated chlorate with excess of titanous salt, titrating back with ferric iron and thiocyanate as indicator. Kikuchi titrated iodate and bromate also, working in all cases at 60°. The results here obtained show that chlorate may be accurately determined at room temperature by the addition of titanous salt at the end-point.

Apparently, chlorate may be titrated with titanium in either sulfuric or hydrochloric acid solution from less than N to more than 4 N. Expts.

⁴ Kikuchi, J. Chem. Soc. Japan, 43, 173 (1922); C. A., 16, 1716 (1922).

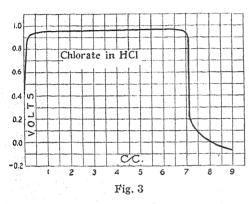
3 and 4, Table III, were carried out in sulfuric, and others in hydrochloric acid. Fig. 3 shows a very great rise in potential, due to hypochlorous acid,

Table III

TITRATION OF CHLORATE WITH TITANOUS ION

 $T_{12}(SO_4)_3$, cc..... 35.52 35.60 35.45 35.60 35.75 35.57 Chlorate factor.. 0.9990 1.0025 0.9920 1.0025 1.0060 1.0010 Av., 0.05 $N \times$ 1.0013

when a little titanium solution is added, then nearly constant voltage, then a very sharp curve to the nearly vertical drop of about 0.8 volt.



The titanous solution was $0.05 N \times 1.407$; 50 cc. of chlorate solution was used in all experiments.

Experiments similar to those with bromate showed, by titration of the iodine set free with thiosulfate, that with the free exit thus provided, not more than 1 part in 600 of the chlorine escaped oxidation in the titration vessel and, hence, when the vessel was closed the chlor-

ine that escaped must have been negligible.

Titration of Ferricyanide with Titanous Ion

The determination of ferricyanide by the potential method seems as simple and accurate as the determination of ferric iron in other compounds. When the solution is concentrated and sulfuric acid is used, a brown precipitate forms near the end of the titration with titanium, but this does not interfere with the end-point.

A solution of pure potassium ferricyanide, determined by the iodine method showed a concentration of $0.05~N~\times~0.7200$. Six titrations with titanium gave a mean for the factor of 0.7201, and the average departures from the mean were +0.0005 and -0.0004.

The author wishes to express his hearty appreciation to Mr. Paul W. Hush and Mr. Neil L. Crone for assistance in this work.

Summary

- 1. Iodate, bromate and chlorate have been determined electrometrically at room temperature by the addition of titanous salt to the solution to the end-point; that is, without adding an excess and titrating back with an oxidizing agent.
- 2. Iodate is best determined in sulfuric acid by the addition of titanium to the solution until the first drop in potential is reached, which marks the

disappearance of the iodate; bromate and chlorate may be determined in either sulfuric or hydrochloric acid by adding titanium to the solution until the final drop which marks complete reduction, is reached.

3. Ferricyanide also may thus be determined electrometrically with titanium as accurately as any other form of ferric iron.

GRINNELL, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 28]

THE CONDUCTANCE OF DILUTE AQUEOUS SOLUTIONS OF HYDROGEN CHLORIDE

By Henry C. Parker¹ Received June 4, 1923

Introduction

In a recent investigation,² Kraus and Parker determined the conductance of iodic acid, using water of various degrees of specific conductance and both glass and quartz cells. If it is assumed that the measurements made in quartz cells with water having a specific conductance of $0.09-0.12\times10^{-6}$ are correct, the presence of an error was demonstrated in the measurements made with water of higher specific conductance and with glass cells. The use of glass cells was shown to influence the results to a somewhat greater extent than the impurities that are present in ordinary "conductivity water." The limiting value for the equivalent conductance of iodic acid, found from the measurements in the quartz cells, was about 0.9% higher than the value found from the measurements in glass cells.

It appeared of interest to confirm the results of Kraus and Parker by carrying out a series of measurements with a typical strong acid in a quartz cell. Hydrochloric acid was chosen, since the equivalent conductance of the chloride ion is known with considerable certainty, and since solutions of this acid may be made by weighing the constituents involved.

Preparation of Materials

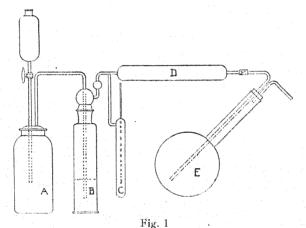
The hydrochloric acid was prepared by means of the apparatus shown in Fig. 1.

In this figure, A is the generating flask; B is a wash bottle, containing "special" sulfuric acid, and C is a trap, introduced to prevent the water in the absorption flask from being drawn back into the generating flask. This trap is likewise filled with "special" sulfuric acid. The absorption flask E is constructed of clear quartz and has a capacity of approximately 1500 cc. D is the drying tube containing phosphorus pentoxide. With the exception of a short piece of rubber tubing, connecting the absorption flask to the drying tube, all connections are of glass. In order to avoid contamination,

¹ National Research Fellow in Chemistry.

² Kraus and Parker, This Journal, 44, 2429 (1922).

no stopcock grease was used on any of the ground-glass joints. The entire apparatus was cleaned and dried, the absorption flask being cleaned with cleaning mixture, live steam, distilled water, and finally with purified air. After drying, the absorption flask was weighed; and after several rinsings about 1000 g. of special conductivity was collected. About 80 g. of a highly purified commercial sodium chloride, which had been purified from insoluble matter by filtration and evaporation of the solution to dryness, was then introduced into the generating flask and the sulfuric acid was allowed to flow upon it. Toward the end of the reaction a small amount of heat was applied to the generating flask, but care was exercised to keep the reaction running smoothly. When the reaction in the flask was completed, the difference in the weight of the absorption flask amounted to about 45 g. and this weight, together with the weight of the water originally introduced into the flask, gave the data necessary for the purpose of calculating the strength of the acid, with the accuracy of a few thousandths of 1%. Both of these



weights were reduced to a vacuum. In this reduction, allowance was made for the change in density of the solution, and thus the difference between these weights gave the weight of the hydrogen chloride reduced to a vacuum.

The acid prepared in this manner had a concentration of approximately 1.4 N. About 150 g. of this concentrated solution was transferred by means of air pressure into a second quartz flask, which contained a weighed quantity (about 1000 g.) of the special conductivity water. The strength of this dilute solution (approximately 0.1 N) was still known to a few thousandths of 1%. This was the solution that was employed in making up the dilute solutions whose conductance was finally measured. The water employed in making up these solutions was prepared in the still described by Kraus and Dexter.⁴ The method of purifying the air as well as other details of manipulation were the same as those previously employed with icdic acid and need not be further described here.

Measuring Apparatus

The apparatus employed in carrying out the electrical measurements was the same as that previously employed by Kraus and Parker. A fre-

³ This purification was ca ried out by Mr. G. F. Des Autels, to whom thanks are also due for checking several resistances and supervising the generation of the hydrogen chloride.

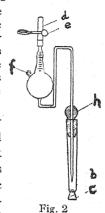
⁴ Kraus and Dexter, This Journal, 44, 2468 (1922).

quency of 1217 was used throughout this investigation at a potential of approximately 7 volts.

The dilute solution, mentioned above, was introduced into the large quartz cell from the weight pipet which is shown in Fig. 2.

All parts of this pipet that come in contact with the acid are constructed of quartz. The capacity is approximately 50 cc. The glass tube b serves the double purpose of centering the pipet over the hole in the stopper of the cell through which the solution was introduced, and of preventing evaporation when the weight of the pipet is being determined. The stopper h into which this glass tube is ground is made of de Khotinsky cement. The flow of the acid solution from this pipet is governed by the pinch clamp e.

The cell used in these measurements is the 3-liter Vitreosil flask called Cell II in the article by Kraus and Parker, a drawing of which is shown in Fig. 3 of that article. In the present investigation, however, the glass tubes, which were used to support the electrodes were replaced by quartz, the seals being made after the manner described by Kraus.⁵ With these new electrodes it



will be called Cell II_d . Owing to the difference in expansion between platinum and quartz, it was impossible to connect the brace across the lower ends of the electrodes to the upper part of the electrode stems, as was done with Cell II. The electrodes were held rigidly, however, by means of 2 heavy platinum wires, crossed nearly at right angles and welded to the small platinum tube leading from the quartz seal. This method gives sufficient rigidity for all purposes.

Intercomparison of Cell Constants

In a recent article, Kraus and Parker showed the presence of an error in the data given by Kohlrausch and Holburn which have been commonly used for the purpose of determining the cell constants in conductance investigations. They suggested the use of the data given by Kohlrausch and Maltby for the specific conductance of potassium chloride, as a basis for this determination, and gave the necessary data for making up these solutions by weight methods. This was the procedure adopted in the present investigation. It was necessary, however, to use auxiliary cells of pipet form in order to calibrate Cell II_d. The constants for these auxiliary cells were determined at 18°, the data for which are found in Table I, while the intercomparison between these and Cell II_d was carried out at 25°.

- ⁵ Kraus, U. S. pat. 1,093,997, 1914.
- 6 Kraus and Parker, This Journal, 44, 2422 (1922).
- ⁷ Kohlrausch and Holburn, "Leitvermögen der Elektrolyte," Teubner, Leipzig, p. 76.
 - 8 Kohlrausch and Maltby, Wiss. Abh. Phys.-Tech. Reichsanst., 3, 180 (1900).

Table I Constants of Standard Cells

· ·	COMPANIATE OF 191	TITLD TAKES WITH THE	
	Cell A	Parallel-series combination	Cell D
Solution I	11.657_{4}	5.94780	3.1507_{2}
Solution II	11.657_{4}	5.9475_{6}	3.1507_{7}
	and the same of th	to a mandature, with part standing to the Wing	# to a consequent any end of the section of the
Av.	11.657_{4}	5.94768	3,15074

The apparatus used in these intercomparison measurements is shown in Fig. 3 of a recent article by Parker. In these measurements, unlike the measurements given in that article, the tube at o, the stopcock at q, and the pinch clamp at p were used in order to break the column of liquid through the tube e, just before resistance measurements were taken. This was accomplished by introducing a slight air pressure into the system at a, when the stopcock q was open.

In the present investigation, 4 pipet cells were intercompared with the Cell II_d . These 4 cells, called Cells A, B, C and D, were connected by means of T-tubes in the neighborhood of d (Fig. 3 mentioned above) and also at the upper part of the stem, where connections were made with the air line. In this manner the 4 cells acted simultaneously when the solution was being mixed. Resistance measurements were taken upon the 5 cells at each of a series of concentrations. Measurements were also made when the pipet cells were connected in series and parallel combina-

TABLE II

INTERCOMPARISON MEASUREMENTS OF CELL IId

Refore Run I

	Belore	e Run 1	
Resistance of Cell II _d Ohms	Cell constant from Cell A	Cell constant from parallel- series combination	Cell constant from Cell D
18,799	0.23163	0.23162	0.23161
41.006	.23121	.23120	23119
96.922	.23088	. 23085	.23086
209.71_{2}	. 230699	. 230657	$.23066_{4}$
601.73_{8}	$.23053_{6}$.230495	$.23047_{7}$
1556.87	. 230585	.230494	$.23050_{9}$
2629.55	.230749	$.23038_{1}$.230538
3637.17	.231167		$.23059_{2}$
7394.41		$.23035_{1}$	$.23082_{0}$
15586.6	artika di kabasa ka di		$.23861_{1}$
	After F	tun I	
537.045	$.23057_{6}$	$.23055_{9}$.230550
2442.07	$.23072_{4}$.230511	.230612
	After R	un II	
242.376	,230717	and the second of the second o	.230580
331.395	.230668	.230610	.230593
1834.26	.230804	$.23060_{0}$.230660

⁹ Parker, This Journal, 45, 1371 (1923).

tions. The results obtained with Cells II_{d} , A and D, and with the parellel-series combination (obtained when B and C are connected in parallel and in series with D) are given in Table II. Cells A, B and C have electrodes of 1 sq. cm. cross section, while Cell D has electrodes of twice this area. Cell A is about 15 cm. in length, while the others are half this length.

In the first column are given the resistances of Cell II_d obtained at each of a series of concentrations of potassium chloride. The data given in the second column have been obtained by dividing the resistance of Cell II_d by the resistance of Cell A, for the same concentration, and multiplying this by the constant of Cell A as found in Table I. The data found in the third and fourth columns have been obtained in a similar manner by making use of the resistances of the parallel-series combination and of Cell D, respectively. The values found in these columns, therefore, represent the apparent "cell constant" of Cell II_d for that particular concentration, when this is determined by intercomparison with the cell in question. These values are plotted against the resistance of Cell II_d in Fig. 3.

Theory for the Variation

A theory to account for the variation in the apparent "cell constant" exhibited in the curves shown in Fig. 3 is outlined in a recent article by Parker. This theory accounts for this variation by the presence of an adsorbed layer in proximity to the electrodes, which has a greater or less resistance than the body of the solution according as the electrolyte is adsorbed negatively or positively, in this layer. This theory appears to be supported by the present investigation. It appears probable that potassium chloride is negatively adsorbed at a platinum surface, while hydrochloric acid is positively adsorbed. 11

Such an absorbed layer would be affected to a considerable extent by the conditions under which measurements were made. First, the resistance of this layer would have a relatively less effect upon the total resistance of the cell if the distance between the electrodes was great. Second, the resistance of such a layer would be inversely proportional to the cross section of the electrodes. Third, the adsorption occurring would be sensitive to factors such as traces of grease, dissolved gases, etc., which would lower the surface tension. Fourth, if we assume that the effect of the alternating current is to "spread out" this layer, it is evident that the "spreading" would be influenced by the voltage and frequency of the alternating current. The first of these phenomena has, in a previous communication, 12 been shown to occur. The occurrence of the second

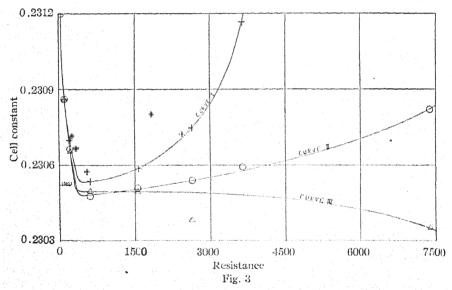
¹⁰ Ref. 9, p. 1378.

¹¹ Pickles, J. Chem. Soc., 119, 1278 (1921). Schilow, Z. physik. Chem., 100, 425 (1922).

¹² Ref. 9, p. 1376.

will be demonstrated in a subsequent article. The third effect has been noted by the writer and was mentioned by Taylor and Acree.¹³ The occurrence of the fourth was mentioned by Kraus and Parker,¹⁴ in their measurements upon iodic acid, where it was found that an increase of voltage caused an apparent increase in the resistance of potassium chloride and a decrease with iodic acid solutions. (A decrease is likewise obtained with hydrochloric acid.) This difference in sign may be accounted for by the difference in sign of the adsorption.

If we have negative adsorption in the case of potassium chloride solution, then the resistance of the adsorbed layers in contact with the electrodes will be greater than that of the body of the solution. Hence the observed resistances in the more dilute solutions may be expected to be greater than the true resistances. Since the "cell constant" is proportional to the resistance of a given solution, such a cell as Cell II_d would exhibit an increasing "cell constant" in the more dilute solutions when intercompared with a cell showing a relatively smaller correction, due to these adsorbed layers. In case the intercompared cell exhibited a relatively greater



correction, then the apparent "constant" of Cell II_d would decrease in the more dilute solutions. Both of these cases may be seen in Fig. 3, where the "constant" of Cell II_d is shown as a function of the observed resistance. Its "constant" has been determined by intercomparison with 3 cells, 2 of which show a relatively smaller correction and the third a greater. Curves I and II, representing the former case, were plotted

¹³ Taylor and Acree, This Journal, 38, 2416 (1916).

¹⁴ Ref. 2, p. 2438.

from the intercomparison data obtained with Cells A and D, respectively, while Curve III, representing the latter case, represents measurements with the parallel-series combination. The large effect obtained when cells are measured in series seems to be characteristic of these phenomena.

The independent and characteristic variation exhibited by the curves in Fig. 3 constitutes one of the strongest proofs that the effect is caused in the cell. It is evident that the measurements at the higher resistances are not at fault, or at least not to the same extent for each cell, since no single correction curve for the higher resistances could possibly be drawn which would reconcile these variations.

Selection of Cell Constant

The effect of such an adsorbed layer would probably become negligible in the more concentrated solutions. In order to determine the constant of a cell, therefore, this would make it advantageous to use as concentrated a solution as possible, providing the resistance is sufficiently high to avoid polarization effects. This condition has been fulfilled in all cases where the standard cells were calibrated directly against the standard potassium chloride solutions, so it is believed that the values given in Table I are accurate. With Cell II_d, however, it is impossible to utilize one of these standard solutions, on account of the presence of polarization at the low resistances which would be obtained. The electrodes of Cell II_d are about 2.3 cm. apart, so it is probable that there will be a considerable correction for the adsorbed layers, at the higher resistances, when potassium chloride solutions are used. It is evident that, if a cell could be found which would give nearly the same relative correction as Cell II_d at a given concentration but which could be calibrated with one of the standards in the more concentrated solutions, the corrections would cancel in the more dilute solutions, where the two cells could then be intercompared. Such a secondary cell is illustrated in the case of the parallel-series combination. It is evident from the curves of Fig. 3 that the Cell D has a somewhat greater correction than Cell IId, while the parallel-series combination has only a slightly smaller correction. Curve III, therefore, is most suitable for the determination of the correct "constant" for Cell IId.

Cell II_d was thrice intercompared with Cells A, B, C and D. The results that were obtained after Run I with hydrochloric acid and at the conclusion of Run II indicated a constant about 0.02% greater than that found in the first series of measurements. This is shown by the points above Curve I, Fig. 3, where the results obtained after Run I are indicated as double crosses and those after Run II as triple crosses. The difference was so small, however, that the same "constant" for Cell II_d was assumed for the two runs, the results of the two intercomparisons being averaged. If we select Curve III to determine the "constant" of Cell II_d,

it is evident from the preceding discussion that the position upon this curve the most likely to give the correct value would be in concentrated solutions, just before the commencement of polarization. When this value was determined from Curve III, a correction of 0.01% was added, on account of the higher value found in the two later intercomparisons. The final value thus selected was 0.23052, which is indicated in Fig. 3. If Curves I or II had been chosen, instead of Curve III, this value would be changed to the extent of about $\pm 0.015\%$.

It is probable that hydrochloric acid is positively adsorbed from the solution in contact with the electrodes. Whether the actual resistance should be greater or less than the observed will depend on two factors. First, the resistance of the adsorbed layer would be less than that of the body of the solution, and if the alternating current is assumed to cause considerable "spreading" of this adsorbed material, the resistance observed might be less than the true resistance. Second, if this adsorption takes place to such an extent that the concentration in the body of the solution is reduced, the observed might be greater than the true resistance. The large volume of the solution (3 liters) surrounding the electrodes of Cell II_d would reduce an error of the latter nature, but in any case it is probable that these factors both are small and partly compensate each other, so it is evident that no correction should be applied to this "constant" when measuring acid solutions. The assumption will be made then that this value remains fixed at 0.23052, for these solutions.

Density of Hydrochloric Acid

The densities of the solutions of hydrochloric acid which were used in these calculations were taken from the data of Cameron and Robinson. These data are plotted in Fig. 4. It is seen that the points at 0.005 and $0.01\ N$ do not coincide with the curve, which is drawn straight down to the density of water at $25\,^\circ$, in the more dilute solutions. These points appear to be somewhat in error, although the other points agree with the results of Reyher¹⁶ for more concentrated solutions, so it is thought that the remaining points are sufficiently reliable. In any case, the corrections for the change of density upon the dilute solutions used in this investigation are almost negligible. The densities were read from the smooth curve shown in Fig. 4.

Experimental Procedure and Results

The experimental procedure was very similar to that employed in the investigation with iodic acid, the principle changes being due to the use of a solution of hydrogen chloride, instead of a solid in order to make up the solutions whose conductance was examined. The water in which the

¹⁵ Cameron and Robinson, J. Phys. Chem., 14, 1 (1910).

¹⁸ Reyher, Z. physik. Chem., 2, 548 (1888).

hydrogen chloride was absorbed and that used for diluting the concentrated solution was drawn from the cell as it was being filled with the conductivity water, and consequently was the best obtainable. The diluted standard hydrochloric acid solution, added to the cell, was allowed to stand in the quartz pipet for an hour before the latter was refilled and weighed. The pipet was handled with great care in order that the weighings should be accurate. The smallest amount of acid solution weighed was 0.6 g., while the weighings were reproducible to better than 0.1 mg. In all, 50 cc. of the dilute acid solution was added to the cell. The neck of the quartz flask serving as a cell was large enough so that this amount of

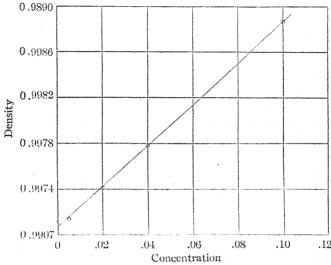


Fig. 4.—Density of HCl at 25°. Cameron and Robinson

liquid made a difference in the height of the solution of about 25 mm. It was experimentally determined that the addition of this amount of solution did not change the "cell constant" appreciably.

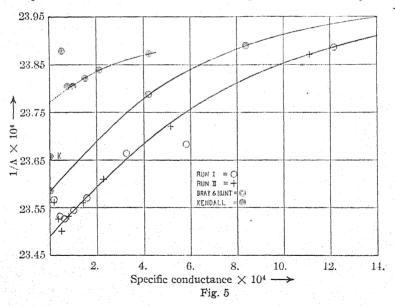
The data obtained in these measurements are given in Table III, where are shown the values of the equivalent conductance and the concentration, the latter of which is expressed in millimoles per liter. The molecular weight assumed for the hydrochloric acid is 36.468. At the bottom are given the weight of water in the cell, the specific conductance of the water, the cell constant, resistance of the leads and the strength of the acid solution that was added to the cell. The latter is expressed as grams of hydrogen chloride (reduced to a vacuum) per gram of solution (weighed in air). The other weights are reduced to a vacuum.

These data are shown in Fig. 5, where $1/\Lambda$ is plotted against $C\Lambda$. The consistency of this work with hydrochloric acid is seen to be nearly as great as that of the results with iodic acid. The impurities in the water are

TABLE III
CONDUCTANCE OF HYDROCHLORIC ACID

	Run I		Run II	
Conen, × 103		Λ		onen. × 10 ³
0.037653_3	424.328	0.0360	126	424.428
$.098305_{3}$	424.957	.0798	498	425.063
.143878	425.05_{1}	.1143	4_5	425.52_{5}
.234084	424.730	.1828	57	424.97_{1}
$.36600_{4}$	424 . 264	.3281	38	424.420
$.76350_{6}$	422.588	, 5329	7_{4}	423.55_{9}
1.3697_{9}	422.24_{0}	1.2123	0	421.58_{3}
2.90414	418.66_{0}	2.6494	0	418.92_{5}
		Wt. HCl (vac.)		
Wt. H ₂ O in vacuum	Sp. cond. H ₂ O	per g, of soln. added	Cell const.	Resist, of leads
Run I 3249.00	0.15×10^{-6}	0.0072783_{6}	0.23052	0.507
Run II 3265.89	$.09 \times 10^{-6}$.00666169	0.23052	0.507

shown to influence the results to a somewhat greater degree than in the case of iodic acid. A possible explanation is that the dilute acid solution becomes slightly contaminated when it is being introduced into the cell. The first two points in each run will have to be neglected, when extrapolating



to infinite dilution, for this reason. The seventh point of Run I is also in error for some unknown reason.

Conductance Data at Round Concentrations

The data given in Table III were plotted on a large scale in order to interpolate the values at round concentrations. $\Lambda_0 - \Lambda$ was plotted against

C. The first two points of each run were neglected, and Runs I and II were weighted as 1:2, which is about the relative precision of two runs carried out in succession in this manner. The values for the concentration expressed in millimoles per liter, the values for the specific conductance, for γ , for K, and for the equivalent conductance, Λ , which were obtained by means of this plot are given in Table V. In the last column are given the average deviations of the experimental points from the interpolated curve, when these points have been weighted as above.

Table IV
Hydrochloric Acid at Round Concentrations

				,	
Concn. $C \times 10^3$	Spec. cond. $L \times 10^3$	γ	$K = \frac{\gamma^2 C}{1 - \gamma}$	Equiv. cond., A	Av. dev.
0.0	0	1.0		425.69	
0.05	0.021274_4	0.999_{53}	0.105	425.489	
. 1	1.042528_{6}	.99905	. 105	425.28_{6}	0.025
.2	$.08497_{66}$	$.9981_{0}$. 105	424.88_{3}	
.3	$.12734_{4}$	$.9971_{6}$. 105	424.48_{1}	.008
.4	$.16963_{3}$	$.9962_{2}$	$.105_{0}$	424.08_{2}	
.5	$.21184_{2}$	$.9952_{8}$	$.105_{1}$	423.68_{3}	.002
.6	$.25398_{1}$	$.9943_{9}$	$.105_{6}$	423.30_{2}	
.7	$.29605_{2}$	$.9935_{1}$. 1064	422.93_{1}	.016
.8	$.33808_{0}$	$.9927_{4}$. 1085	422.60_{0}	
.9	$.38004_{2}$	$.9920_{1}$.1108	422.29_{1}	
1.0	421997	$.9913_{2}$. 1131	421.997	.085
2.0	$.8397_{35}$	$.9863_{2}$. 1421	419.86_{7}	• • .
3.0	1.255_{63}	$.983_{21}$	$.172_{6}$	418.54	.005

In Table VI are found the values at round concentrations for iodic acid, from the work of Kraus and Parker. The for this interpolation the values of $\Lambda_0 - \Lambda$ were plotted against C, for the more dilute solutions, while Λ was plotted directly against C in the more concentrated. Run 1 was neglected, and Runs 2, 3, 4 and 5 were weighted in proportion to the numbers 1:2:3:4 which is, again, about the relative precision of a series of measurements carried out in this manner. Runs 6 and 7 were weighted as 1:2, over the part of the concentration range covered by these runs. The first two points in Runs 6 and 7 were neglected for reasons given in that article. The data given in Table VII (Kraus and Parker, Run 10) obtained in glass cells, are used for the interpolation below $0.01\ N$, where the concentration is high enough so that the impurities in the water and alkali from the glass do not measurably affect the results.

The average deviations of the experimental points from the interpolated curve are again given in the last column when weighted as above. If the different runs are not weighted, these deviations will, of course, be

¹⁷ Ref. 2, pp. 2439-40. In Table VI, p. 2439 the data given for the concentrations of Run 7 are expressed in moles per liter instead of millimoles, as indicated at the top of this table.

increased, but the values given in this column are very close to the values which would be found by using the more precise of the runs and neglecting

TABLE V

IODIC ACID AT ROUND CONCENTRATIONS

	lodic Ac	id at Rou	ND CONCENTE	RATIONS	
Conen. C X 10 ³	Spec. cond. $L \times 10^3$	γ	$K = \frac{\gamma^2 C}{1 - \gamma}$	Equiv. cond.,	Av. dev.
0		1.0		389.55	
.01	0.003894_{96}	.99985	0.07_{17}	389.49_{6}	
.02	$.007788_{84}$.99971	$.07_{17}$	389.44_{2}	
.03	$.011681_{6}$.99957	$.07_{17}$	389.387	
.04	$.015569_{3}$	$.999_{43}$	$.07_{17}$	389.23_{3}	
.05	$.019463_{9}$	$.999_{29}$	$.07_{17}$	389.279	0.022
.06	$.023347_{5}$	$.999_{15}$.0717	389.22_{5}	
.07	$.027242_{0}$	$.999_{02}$	$.071_{7}$	389.17_{1}	
.08	$.031129_{3}$	$.998_{87}$.0717	389.11_{6}	
.09	$.035015_{6}$	$.998_{73}$.0717	389.06_{2}	
.1	$.038900_{8}$	$.9985_{9}$	$.071_{7}$	389.00_{8}	.018
.2	$.07769_{f 40}$	$.9972_{1}$.0717	388.47_0	
.3	$.11638_{0}$.99584	.0717	387.93_{4}	.002
.4	$.15496_{0}$.99447	0717	387.40_{1}	
.5	$.19343_{0}$	$.9931_{4}$.0719	386.87_{9}	.013
.6	$.23181_{7}$	$.9918_{0}$.07209	386.36_{1}	
.7	$.27010_{2}$.99051	.07250	385.86_{0}	.009
.8	$.30830_{4}$	9892_{8}	$.0731_{4}$	385.38_{0}	
.9	$.34642_{6}$,98809	$.0739_{0}$	384.918	.005
1.0	$.38448_{0}$	$.9869_{8}$	$.0748_{4}$	384.48_0	.003
2.0	$.7609_{20}$	$.9766_{7}$.08175	380.46_{0}	
3.0	1.13115	$.9679_{2}$	$.0876_{0}$	377.05_{2}	.019
4.0	1.4962_{8}	$.9602_{6}$	$.0928_{2}$	374.07_0	
5.0	1.8568_{3}	$.9533_{2}$	$.0973_{5}$	371.36_{6}	. 027
6.0	2.2130_{7}	$.9468_{2}$	$.1012_{0}$	368.84_{5}	
7.0	2.5653_0	$.9407_{6}$	$.1045_{7}$	366.47_2	.008
8.0	2.9141_2	$.9350_{9}$	$.1077_{7}$	364.26_{5}	
9.0	3.2596_{5}	$.9297_{5}$	$.1108_{6}$	362.18_{4}	.004
10.0	3.6018_{4}	$.9246_{2}$	$.1134_{1}$	360.184	.006
20	6.870_{4}	$.8818_{4}$	$.1316_{2}$	343.52	
30	9.966_{3}	$.8528_{0}$.14823	332.21	.043
40	12.805	$.8218_{2}$	$.1516_{2}$	320.14	
50	15.554	$.7985_{9}$	$.1583_{2}$	311.09	.005
60	18.192	$.7783_{3}$	$.1639_{8}$	303.20	
70	20.735	$.7604_{2}$	$.1689_{4}$	296.22	.007
80	23.190	.74414	$.1731_{4}$	289:88	
90	25.567	$.7292_{5}$.17678	284.08	.01
100	27.873	$.7155_{2}$.17997	278.73	.01
200	48.504	$.622_{56}$	205_{38}	242.5_{2}	
300	65.95_{5}	$.564_{34}$	21933	219.8_{5}	.03
400	81.76	524_{4}	.2316	204.4	
500	95.85	$.492_{1}$.2384	191.7	.15
			-		

the others. For that reason these values represent the true precision of the interpolated results more nearly than the values obtained by giving equal weight to the different runs. It may be mentioned that these interpolated results agree, in the more concentrated solutions, with the work of Ostwald¹⁸ and Groschuff¹⁹ upon iodic acid, well within the limits of their experimental error. This fact gives a check upon the values of the cell constants used in these measurements.

Discussion

The experimental values of $1/\Lambda$ and $C\Lambda$ obtained in the two runs with hydrochloric acid are plotted in Fig. 5. In comparison with the similar curve for iodic acid, given by Kraus and Parker, ²⁰ it is seen that the form of the curve is very similar in the two cases. The slope of the curve for hydrochloric acid is less steep, showing the latter to be the more highly ionized, but the concentration range over which the measurements approximate a straight line, within the experimental error, is nearly identical. This type of curve may thus be considered the general form holding for solutions of strong acids. It is evident that such acids obey the mass-action law to a much closer approximation in the very dilute solutions than is the case with the inorganic binary salts.

The value for the equivalent conductance at infinite dilution obtained from this curve is 425.69. If the value for Λ_0 for the chloride ion at 25° is assumed to be 75.8, as found by Noyes and Falk, 21 this will give a value of 349.89 for the limiting value of the hydrogen ion at 25°. The corresponding value obtained with the iodic acid was 349.93. It is evident that this check is even better than could be reasonably expected, although these numbers are based, in reality, upon the relative values of Noves and Falk for the Λ_0 of the iodate ion at 18° and the chloride ion at 25°,22 and thus these measurements constitute a check upon these relative values. The greater chance for a discrepancy between the work with iodic acid and hydrochloric acid, however, consisted in the determination of the cell constants, in the two cases. When the cell constants were determined in the investigation with iodic acid, it was not recognized that these quantities varied with the concentration in the case of some electrolytes, and it was more by accident than intention that the determination of this quantity was made in the neighborhood of the minimum of the cell constant curve for Cell II, when intercompared with the standard cell. The accurate method of intercomparison used in the present investigation had not then been devised and, since the measurements in the more dilute

¹⁸ Ostwald, J. prakt. Chem., [2] 32, 300 (1885).

¹⁹ Groschuff, Z. anorg. Chem., 47, 331 (1905).

²⁰ Ref. 2, p. 2442.

²¹ Noyes and Falk, This Journal, 34, 454 (1912).

²² Thus, in the work with iodic acid the value for Λ_0 of the iodate ion, at 25°, was experimentally determined with considerable precision, in terms of the value given by Noyes and Falk, for 18°.

solutions were inconsistent, there was no other choice than to accept the measurements made in the neighborhood of this minimum point. The degree of precision obtained in these two investigations, which is indicated by the values for the average deviations from the interpolated curve, would indicate, of course, that a check of this order of magnitude might be expected.

The value of the mass-action constant, corresponding to the straight line drawn in the more dilute solutions of Fig. 5 is 0.105, while the corresponding value for iodic acid was found to be 0.0717. Whatever other significance these values may have, it is probable that at least they measure the relative "strength" of these acids.

Work of Other Investigators.-Hydrochloric acid has been the subject of several important investigations, although no two of the investigations show agreement at infinite dilution. Most of the investigations have been carried out at 18°, but these may be compared with the measurements at 25°, with the aid of a few assumptions. Thus, the difference in the Λ_0 values for the hydrogen ion at 18° and 25° was found experimentally by Kraus and Parker to be 34.31; while the difference between the corresponding values for the chloride ion given by Noyes and Falk, is 10.3, giving a total of 44.6 to be added to the value of Ao for the hydrochloric acid at 18° in order to transform this value to that for $25^{\circ}.^{23}$ When this quantity is added to the values of Λ_0 at 18° . the following values are obtained at 25°, for the two most accurate investigations: Goodwin and Haskell, 24 - 424.7; Noyes and Cooper, 25 - 423.6. The values obtained in the investigations made at a temperature of 25° are as follows: Bray and Hunt, 26 -424: Kendall. 422.7. The values obtained are seen to vary between 422.7 and 424.7. for the Λ_0 of hydrochloric acid at 25°. All of these investigations were made with glass cells and conductivity water of only a fair degree of purity. In none of these investigations were the solutions made up by weight methods, a procedure that has been accomplished in the present investigation.

Conclusion

The results of Kraus and Parker with iodic acid in glass and quartz cells and with water of various degrees of purity would indicate that, except for experimental error, the investigations mentioned in the pre-

 23 It is believed that this value of 44.6 is relatively accurate, since the relative values of Λ_0 at 18° and 25° are known to a greater degree of precision than the absolute values. Thus, if the value given by Bates [This Journal, 35, 534 (1913)] or by Washburn [This Journal, 40, 158 (1918)] had been chosen for the Λ_0 of the iodate ion at 18°, instead of that of Noyes and Falk, the Λ_0 values of the hydrogen ion, determined by Kraus and Parker at 18° and 25° would both have been increased to the extent of 0.1 or 0.2, respectively, while the difference between these values at 18° and 25° would have remained unchanged. Similarly, the difference in the values of Λ_0 for the chloride ion at 18° and 25°, as found by the extrapolation method used by Bates and Washburn, would agree closely with the value 10.3 obtained by Noyes and Falk.

- ²⁴ Goodwin and Haskell, Phys. Rev., 19, 369 (1904).
- 26 Noyes and Cooper, Carnegie Inst. Pub., 63, 137 (1907).
- ²⁶ Bray and Hunt, This Journal, 33, 787 (1911).
- ²⁷ Kendall, *ibid.*, **39**, 13 (1917).

ceding paragraph should give a value of Λ_0 approximately 0.9% low.28 This should vary, however, with the circumstances surrounding the investigations. Thus Goodwin and Haskell used a cell of which the greater part was of platinum, and employed two different methods of correcting for the impurities in the water, so it is evident that their determination should be but slightly lower than the value found in the present investigation. Bray and Hunt, whose calculated values are indicated in Fig. 5, used the results of Goodwin and Haskell for extrapolation, so these results should likewise, be, close. Both of these conditions are fulfilled. The results of Noves and Cooper and of Kendall, of which the latter are shown in Fig. 5, are 0.5% and 0.7% lower, respectively, than the results obtained in the present investigation. The value of Λ_0 given by Kendall, however, is not obtained by extrapolation but by adding the limiting value for the chloride ion to a value of the hydrogen ion previously obtained. The value 422.7, obtained in this manner, is indicated in Fig. 5 at a point considerably below his experimental results and marked "K." An extrapolation such as indicated by the dotted line would give a result of 420.7, showing difference of 1.2% from the results obtained in the present investigation. The value for the mass-action constant, determined from this extrapolation, would be about 0.08 higher than that obtained in the present investigation. Thus, it is indicated that the results of other investigators confirm the conclusions reached by Kraus and Parker regarding the effect of (1) the impurities in the water and (2) the use of glass cells upon the conductance of an acid solution.

It is interesting to note that the impurities of the water in the investigation by Kendall are apparently of a different nature from those obtained in the present investigation. This is seen by the sharper minimum in his experimental results. The next experimental point in the more dilute solutions would come far above the plot. The slope of the line given by Bray and Hunt's calculated values is nearly identical with that obtained in the present investigation. This fact would tend to support the expedients employed by Goodwin and Haskell for the elimination of the effect of the impurities in the water. The actual experimental values obtained by Bray and Hunt are far above the plot and cannot be indicated. It appears, however, that their curve would coincide with the curve obtained in the present investigation, if these were extended to the more concentrated solutions.

The value of Λ_0 for the hydrogen ion obtained in this investigation is based upon a somewhat firmer foundation than the value obtained with

Upon extrapolating to infinite dilution the results for iodic acid in a glass cell, 386.04 is found for Λ_0 , a value 0.9% lower than for the results in quartz cells. The corresponding value of the mass-action constant is 0.05 high.

iodic acid, due to the greater certainty in the determination of the cell constant. Heretofore, the values of Λ_0 for the other ions were known to a considerably greater degree of accuracy than was the case with the hydrogen ion. These two investigations upon iodic acid and hydrochloric acid seem to have reversed the situation. The extrapolation of the results with strong acids appears to be somewhat more safely accomplished, due to the fact of closer conformity to the mass-action law. Until the values for the chloride and iodate ions are known with a greater degree of accuracy, there is small purpose in giving the value for the hydrogen ion to more than one decimal place. However, if it is assumed that the value for the chloride ion at 25° is 75.8, the most probable value for the hydrogen ion appears to be 349.89 \pm 0.05. This number will, of course, represent a lower limit to this value, due to the method of extrapolation.

Summary

- 1. The conductance of aqueous solutions of hydrochloric acid has been determined at 25° between the concentrations of 0.04 and 3.0 millimoles per liter. The solutions were made up by weight methods to an accuracy of a few hundredths of 1%. Water was used having a specific conductance of the order of 0.1×10^{-6} .
- 2. The values for the equivalent conductance show a slight maximum in the neighborhood of 0.1 millimoles per liter, due to the influence of the impurities in the water, which apparently cause a somewhat greater effect than in the case of iodic acid.
- 3. Comparison with the results of other investigators confirm the conclusions of Kraus and Parker regarding the considerable influence of the impurities in the water and of the alkali in glass cells upon the conductance o dilute acid solutions.
- 4. Values at round concentrations have been interpolated from the results upon hydrochloric and iodic solutions. The data for iodic acid are given from $0.05 \times 10^{-3} \ N$ to $0.5 \ N$.
- 5. The "cell constant" was determined by an intercomparison with 3 standard cells, over a considerable range of concentrations with potassium chloride as the electrolyte. The unusual results of this intercomparison may be explained by assuming the presence of an adsorbed layer (in contact with the electrodes) whose resistance is greater or less than that of the body of the solution, according to whether the electrolyte is negatively or positively adsorbed. One of the intercompared cells apparently has a greater correction for this "adsorbed layer" than the cell used in the measurements with the hydrochloric acid, while the other two have a smaller correction. On the supposition that hydrochloric acid will be positively adsorbed and will consequently have but slight correction for this effect, a value for the "constant" is selected at the minimum point of

the "cell constant" curve, which value is assumed to remain fixed in the measurements with the acid solutions.

6. Extrapolation of the results upon the assumption that the mass-action law is approached as a limiting form at infinite dilution, gives a value of Λ_0 for hydrochloric acid of 425.69. Assuming that the value of Λ_0 for the chloride ion at 25° is 75.8, a value of 349.89 for the hydrogen ion at that temperature is obtained. By comparing this with the value 349.93 obtained by Kraus and Parker for iodic acid, the value 349.89 \pm 0.05 is deduced as the most probable value for the hydrogen ion at 25°—the basis for the "cell constant" being more firmly established in the measurements with hydrochloric acid. The mass-action constant corresponding to this extrapolation has a value of 0.105.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. VI. METALLIC GERMANIUM. REDUCTION OF GERMANIUM DIOXIDE. PREPARATION OF FUSED GERMANIUM. PHYSICAL AND CHEMICAL PROPERTIES

By L. M. Dennis, Katharina M. Tressler and F. E. Hance² Received June 4, 1923

Material.—The germanium that was used in these investigations was prepared by the reduction of pure germanium dioxide that was practically free from other metals, including arsenic.³

Dehydration of Germanium Dioxide

Since it was desirable that germanium dioxide be thoroughly dehydrated before experiments were made upon its reduction, the lowest temperature at which complete dehydration resulted was ascertained by heating germanium dioxide that had been dried at about 100° to successively higher temperatures until constant weight was obtained. It was found that the dioxide is completely dehydrated when heated to a temperature of 950° for about 3 hours, and that there is no volatilization of germanium dioxide at a temperature of 1250°. The dehydration may be effected rapidly by heating the oxide over a gas-air blast flame, and the product that is formed is not hygroscopic.

- ¹ This article is based upon the theses presented to the Faculty of the Graduate School of Cornell University by Katharina M. Tressler and F. E. Hance in partial fulfilment of the requirements for the degree of Doctor of Philosophy.
- ² The experimental work of this investigation was carried on separately and not jointly by Miss Tressler and Mr. Hance.
- ³ Dennis and Papish, This Journal, 43, 2131 (1921). Dennis and Johnson, ibid., 45, 1380 (1923).

Reduction of Germanium Dioxide by Aluminum

The heat of formation of aluminum oxide is far greater than that of silicon dioxide or of stannic oxide, and since germanium lies between silicon and tin in the fourth group of the Periodic Table, it is clearly apparent that metallic aluminum will easily reduce germanium dioxide.

Forty g. of germanium dioxide and 14 g. of granular aluminum were mixed and placed in a small iron crucible that was thickly lined with aluminum oxide. The reaction was started with an ignition mixture of magnesium and barium dioxide and proceeded quietly through the mass. A dense white cloud was, however, given off, and this was found to consist chiefly of germanium dioxide. A button of bright, lustrous metal was obtained, but as this represented a yield of only 61%, further study of this reaction was abandoned for the present.

Reduction of Germanium Dioxide by Hydrogen

Winkler⁴ found that germanium dioxide is reduced by hydrogen at red heat but that the reduction is not always complete.

Müller⁵ stated that the ratio GeO₂:Ge was not suited to the determination of the atomic weight of germanium, both because of impurities in the germanium oxide that he used, and because of loss that he thought resulted from the formation and escape of germanium hydride.

In our study of this reaction, the following procedure was employed. A small sample of germanium dioxide that had been dehydrated at about 950° was weighed into a porcelain boat which was heated to definite temperatures in hydrogen. The hydrogen was first passed through spirals of redhot copper gauze and then through drying towers filled with calcium chloride. A quartz tube drawn out to a fine tip was joined to the exit end of the quartz combustion tube.

After the air in the apparatus had been displaced by hydrogen, the temperature of the combustion furnace was slowly raised. At 500° the surface of the white germanium dioxide began to turn gray, and when the temperature had risen to 540° , the whole surface of the dioxide had taken on this gray color. The temperature was maintained at this point for 45° minutes, the powder changing in that time to a very dark gray. The heat was then turned off, the boat was allowed to cool in hydrogen, and the hydrogen was displaced by air. The weight of the boat showed that reduction was not complete. It was, therefore, re-inserted in the combustion tube and heated in hydrogen for 90° minutes more at from 500° to 540° . The weight of the residual germanium now coincided with the calculated amount (at. wt., Ge = 72.5).

⁴ Winkler, J. prakt. Chem., 142, 177 (1886); 144, 188 (1887).

⁶ Müller, This Journal, 43, 1085 (1921).

	G.
Wt. GeO ₂ taken	0.3498
Heated in hydrogen at 500-540° for 45 minutes, loss	.0909
90 minutes longer, additional loss	.0162
Total loss in 2 ¹ / ₄ hours	.1071
Calculated loss in weight, GeO ₂ —Ge	.1071

The boat and its contents were then heated for $2^{1}/_{4}$ hours longer in hydrogen at 500-540°, and the temperature was finally raised to 900°. No change in weight resulted.

During the reduction of the oxide, a porcelain dish was repeatedly held in the hydrogen flame burning at the quartz tip, but at no time was there formed a mirror of metallic germanium nor did any deposit appear within the quartz combustion tube beyond the boat. The above results indicate that a comparatively small amount of germanium dioxide is quantitatively reduced by about 2 hours' heating in hydrogen at 540° , and that no volatilization of germanium or of any compound of the element takes place under these conditions.

Metallic germanium prepared in this manner is a dark gray powder without metallic luster.

When, however, attempt was made to reduce larger amounts of germanium dioxide that completely filled 4 porcelain boats, there appeared on the walls of the quartz tube beyond the boats a deposit that was black nearest the heated area, and shaded off through brown to yellow toward the cold end of the tube.

Total charges of from 10 to 14 g. always yielded an amount of germanium that was below the calculated quantity.

Preparation of Fused Germanium

A preliminary trial of Winkler's method⁴ of fusing powdered germanium, prepared by reducing germanium dioxide in hydrogen under a layer of borax glass showed that a small amount, about 1 g., could be fused to a bead that was free from boron and sodium. When, however, a larger sample of 26 g. of germanium was heated with 30 g. of borax glass in a covered porcelain crucible over the blast lamp to a temperature of about 930°, the germanium did not coalesce. About 5% of boric acid was then added to a fresh portion of this mixture, and upon fusion there resulted small granules of germanium from 1 to 3 mm. in diameter which were coated with a black powder. The flux also was deep black in color, and when digested in water it yielded a reddish-brown, flocculent residue, consisting chiefly of hydrated germanous oxide.

When the cover of the crucible was lifted during the heating of powdered germanium under borax glass, a white cloud of germanium dioxide rose from the crucible. This misled Winkler into believing that the "vaporization temperature of germanium lies only slightly above its melting point."

As a matter of fact, metallic germanium, as will be shown later, is not volatile at a temperature 300° above its melting point, and the white cloud that rose from the open crucible is doubtless due, as Biltz⁶ has also pointed out. to oxidation of volatile germanous oxide that is formed by the action of molten borax upon germanium.

Powdered germanium was next fused under a layer of anhydrous sodium sulfate. Small samples yielded bright, silvery granules of germanium and a larger sample, about 40 g. of germanium, gave a button of brilliant luster that was distinctly crystalline in character. The button was surrounded by a vellow, transparent, glass-like material that evolved hydrogen sulfide when treated with hydrochloric acid and contained 48.94% of germanium. The weight of the button was only 73.8% of the powdered germanium that was used.

Some of this metal from the first fusion was again fused under sodium sulfate at temperatures rising from 829° at the beginning to 1050° at the end of the 10 minutes' heating. Reduction of the sodium sulfate again resulted and the metallic regulus weighed only 77.7% of the fused germanium that was employed.

These results made it clear that salts of oxy-acids are not suitable as fluxes for this purpose. The compound that is employed as a flux should have a somewhat lower melting point than germanium, but should not appreciably volatilize or dissociate at a temperature that would ensure fluidity of the metal. Sodium chloride seemed to meet these requirements.



Fig. 1.—(Actual size)

A porcelain crucible 7 cm. in diameter was charged first with a layer of pure, dry sodium chloride to a depth of about 15 mm., then with a layer of a mixture of equal parts of salt and powdered germanium that had been ground together, and finally with salt nearly to the top. It was then covered and placed upon a short, perforated cylinder of asbestos board which rested on an iron ring. The crucible was surrounded by 3 concentric tubes of asbestos board through the walls of which passed a long asbestos

tube which permitted the reading of the temperature of the crucible by means of an optical pyrometer. The crucible was heated by the direct flame of 2 blast lamps, and the temperature was brought to from 980° to 1000° and was held there for about 30 minutes. The crucible was

⁶ Biltz, Z. anorg. Chem., 72, 313 (1911).

allowed to cool and was then broken. The germanium was found as a single, brilliant, crystalline button. (Fig. 1.) Adhering salt was removed by digesting the metal in hot water. This solution was alkaline, probably because of the presence of sodium germanate which resulted from the fluxing off of the small amount of the oxides of germanium in the powdered metal. The yields from 3 fusions, in which 24, 38 and 41 g. of powdered germanium were used, were 96%, 96.05% and 96.30%, respectively. Are spectrograms of the preparations showed that they were free from other metals.

Behavior of Germanium when Heated in Hydrogen

Müller states⁵ that germanium dioxide is completely reduced to the metal by heating in hydrogen to 700°, but that there is always loss of weight when the metal is further heated in hydrogen at the above temperature. In a later article⁷ he adds that "metallic germanium is slowly but appreciably volatile in hydrogen at elevated temperatures," and he gives these temperatures as 750–800°. He ascribes the loss in weight to the direct formation of a volatile hydride, the evolution of which was indicated by the formation of a slight black precipitate when the escaping hydrogen was "passed through a solution of a silver salt." He gives no description of his method of preparing metallic germanium, nor of the manner in which its purity was tested.

Since it seemed possible that the loss in weight of germanium when heated in hydrogen, as reported by Müller, might be due to the presence of oxides of germanium in the metal and the consequent volatilization of germanous oxide, detailed experiments were made with the object of first freeing the germanium from all trace of oxide and then heating this product in pure hydrogen to ascertain whether loss in weight and the formation of a volatile hydride resulted.

The germanium that was used was prepared by reduction of very pure germanium dioxide in hydrogen, fusion of the powdered germanium under pure sodium chloride, pulverizing the fused germanium and repeating the fusions under salt until the solution of the flux proved to be neutral to litmus. The final button was pulverized, the powder was digested several times in boiling water to remove the salt, and the product was then heated for 8 hours at 1000° in a current of carefully purified hydrogen.

A sample of this metal weighing 8.93 g. was placed in a porcelain boat which was then inserted in a quartz tube that rested in a combustion furnace. Hydrogen prepared by electrolysis was passed through a purifying chain containing, in the order given, alkaline potassium permanganate, calcium chloride, concd. sulfuric acid, platinized asbestos heated to 260°, soda lime, calcium chloride, concd. sulfuric acid and phosphorus pentoxide.

⁷ Müller, This Journal, 44, 1909 (1922).

The hydrogen then entered a Y-tube, part of it passing through the quartz combustion tube, and the remainder directly through two Wagner absorption flasks containing a $0.25\ M$ solution of silver nitrate. The hydrogen issuing from the quartz tube passed through a small tube with 3 constrictions, and then through 2 Wagner flasks containing a solution of silver nitrate of the above-mentioned concentration.

After the air in the apparatus had been displaced by hydrogen, the germanium was heated to 760–800°. The temperatures were measured by a thermocouple, the hot junction of which was in the quartz tube directly beside the boat.

In the first run, the solution of silver nitrate in both pairs of Wagner flasks was blackened and a small amount of germanium was found in the flasks connected to the combustion tube. The constricted tube was not heated during this first experiment. Since the silver nitrate was reduced not only by the hydrogen that passed over the germanium but also by that which came directly from the purifying chain, 2 spiral gas-washing bottles containing a $0.25\,M$ solution of silver nitrate were inserted at the head of the chain and the metal was then heated in the current of hydrogen on 5 successive days. The introduction of silver nitrate into the purifying chain stopped the reduction of the silver nitrate by the hydrogen that entered it directly from the chain.

The run, each day, consisted in first passing the hydrogen over the germanium at 760-800° for from 2 to 4 hours (see Table I) and through the heated, constricted tube and the solution of silver nitrate beyond, then allowing the furnace to cool, weighing the germanium and the constricted tube and testing the silver nitrate for germanium. The germanium was then replaced in the quartz tube, the apparatus was connected, air was swept out by hydrogen, and the temperature of the furnace was raised to 960-1000° to melt the germanium in the boat. The furnace temperature was then lowered until the germanium solidified, and was then immediately raised again until the metal melted. The metal was in this manner alternately melted and solidified about 10 times each day with the object of repeatedly exposing fresh surfaces of it to the action of hydrogen and thus gradually reducing all oxide of germanium that might be present. During the first 3 days, the germanium lost weight, but the loss steadily became less. There was a correspondingly decreasing amount of germanium deposited in the heated, constricted tube, but no reduction of silver nitrate was observed after the first day. Four hours' heating on the fourth day gave no loss in weight of germanium and no evidence of germanium passing out of the combustion tube. For the fifth day's run, a new quartz tube was used so that the formation of a deposit in the tube beyond the boat, which would be due to the presence of germanous oxide, might clearly be observed. No such deposit was seen, the germanium did not lose weight, no deposit

was formed in the constricted tube, and no reduction of the solution of silver nitrate resulted.

When, however, hydrogen was passed over *molten* germanium the metal invariably lost weight and germanium was found in the flask that contained the solution of silver nitrate.

Table I

Results Obtained when a Sample of Germanium Was Heated in Hydrogen

Day	Duration of heating each day 760-800° Hrs.	Total duration of heating 760-800° Hrs.	Loss in weight of germanium G.	Gain in weight of constricted tube G.	Germanium present in AgNO ₃ solution
1	3	3	0.0090	Tube broke	Trace
2	2	5	.0066	0.0054	None
3	4	9	.0020	.0004	None
4	4	13	.0000	.0000	None
5	4	17	.0000	.0000	None

The above experiments seem to warrant the conclusion that metallic germanium which is free from oxide does not lose weight when heated in hydrogen to a temperature not exceeding 800°, but that volatilization of germanium does take place when hydrogen is passed over the molten metal.

The Physical Properties of Germanium

Melting Point.—Determinations of the melting point were made by melting the metal in a graphite crucible that rested in an electric-resistance furnace, measuring the temperature by means of a platinum-platinumrhodium couple and a potentiometer indicator, and plotting the cooling curve. The metal was purified by several fusions under pure sodium chloride and then repeatedly melting and cooling it in a current of hydrogen. It was finely pulverized and 105 g. of it was packed in the graphite crucible around the quartz protection tube of the thermocouple, being firmly tamped down to exclude air as completely as possible. crucible was next filled to the top with tightly packed sugar carbon, placed in the electric furnace and heated to about 980°. The current was then turned off, and temperature readings were made at 1-minute intervals as the metal cooled. A constant value of 958.5° was obtained over a period of 10 minutes. Repetition of the determination gave the same result. The germanium was then removed from the crucible, pulverized, melted in a current of hydrogen, again pulverized, and its melting point redetermined as above. The results were identical with the first value. An arc spectrogram of the metal was then made and the material was found to be free from impurities.

The Sprouting of Germanium.—When germanium is melted and is then quickly cooled, the "sprouting" of the metal, as noted both by Winkler and by Biltz, 6 is very pronounced. Winkler ascribes the phenomenon to

the great increase in volume of the metal when it crystallizes from the molten condition.

In one of our early experiments, 1 g. of the powdered metal, when fused under borax, solidified to a small button about 4 mm. in diameter, from the top of which projected a cone-shaped protuberance with a needle-sharp point about 3mm. high. When a larger amount, about 30 g., was fused under sodium sulfate and more slowly cooled, there resulted a circular regulus about 40 mm. in diameter and 10 mm. thick, from the middle of the upper surface of which there had been extruded a mass about $^{1}/_{4}$ the size of the main button. The whole surface was beautifully crystalline.

When germanium was melted in a small porcelain boat in an atmosphere of nitrogen, it was found that the sprouting along the surface was very prominent. It was noticed that when the heating was stopped and the asbestos housing around the quartz tube was removed, the metallic germanium retained its redness after the quartz tube and the porcelain boat had resumed normal appearance. The metal then gradually darkened, but suddenly there appeared within the ingot one or two bright spots which rose to the surface and then, with the suddenness of the bursting of a bubble, became dark. This observation seems to support Winkler's explanation of the "sprouting" of germanium. The exterior of the molten metal cools and solidifies first, and when the molten interior solidifies, the resulting expansion of the metal causes it to burst through the surrounding shell. This usually occurs on the upper surface where the shell is thinnest. When the regulus is slowly cooled from the molten condition, the sprouting is much less pronounced and the surface of the metal then shows a beautiful, coarsely crystalline structure.

Since it was possible that the sprouting of germanium might be due to absorption of the gas in contact with which it was melted and the expulsion of this gas upon solidification, as is the case with silver when melted in an atmosphere of oxygen, the metal was melted in a porcelain crucible that rested in a special, closed steel crucible which was exhausted of air. The steel crucible was then cooled as quickly as possible, and although the sprouting was not so marked as when the chilling was more rapid, 3 large protuberances appeared on the sides of the button. Winkler's explanation of the sprouting of the metal, therefore, appears to be correct.

Specific Gravity.—Crystalline germanium that had carefully been purified for the determination of the melting point (see above) was melted in porcelain boats in hydrogen in such a manner as to yield small, compact globules of the metal about 2 mm. in diameter. Two pycnometers were used, one of 10cc. capacity and the other of 25 cc. After the germanium and water had been placed in the pycnometer, the instrument was placed in a desiccator under diminished pressure for several hours. The results of the two determinations were the same, d_{20}^{20} , 5.35. This value agrees very

closely with that obtained by Dr. Albert W. Hull who used a sample of the same preparation of germanium. He wrote: "The density given by X-ray analysis is 5.36. This is correct within one-half of one per cent., and should agree with the density found by other methods for chemically pure germanium free from holes."

Hardness.—Metallic germanium is extremely brittle. However, attempts to determine the hardness of crystalline germanium were kindly made for us by Professor H. Diederichs. Both the Brinell test and the Shore Scleroscope hammer test were separately applied to blocks of polished germanium. In both cases the metal was so thoroughly shattered that even approximate estimation of the hardness could not be made.

A compact specimen of very pure germanium, weighing about 12 g., was then submitted to Professor A. C. Gill, who found that it scratched a well crystallized piece of adularia, but made no mark on epidote. This fixes its hardness number between 6 and 6.5 at, say, 6.25.

Crystal Form.—When a considerable amount of germanium is fused in a large porcelain crucible under a thick layer of salt and is slowly cooled it shows beautiful crystallization on the upper surface. Professor A. C. Gill examined the preparation shown in Fig. 1, and states that it is an aggregate of elongated crystals that are bounded in some cases by octahedral faces. Some of the crystals exceed 3 cm. in length, and occasionally are notched or covered with small dendritic branches. He adds that this particular form of surface crystallization seems to be peculiar to germanium, although it resembles to a certain degree that of antimony.

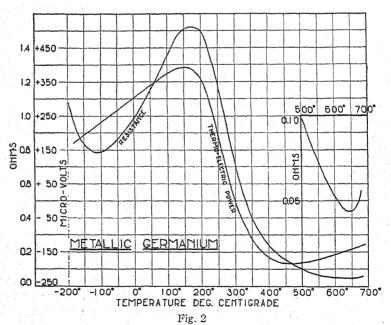
Electric Resistance and Thermoelectric Power.—For the determination of these two values it was necessary to prepare a small bar of germanium about $25 \times 5 \times 5$ mm. This was first attempted by fusion of the metal in a small porcelain boat in an atmosphere of nitrogen. The cool ingot, however, adhered tenaciously to the porcelain, and the bar of germanium could not be removed without fracture because of the very great brittleness of the metal.

To obviate this difficulty, the boat was lined with a paste of germanium dioxide which was then thoroughly dried. The boat was filled with powdered crystalline germanium and was heated in nitrogen in a quartz tube as before. When the temperature of the melting point of germanium was reached, the tube filled with a thick, dark colored vapor. Heating was at once stopped, and examination of the contents of the tube after cooling showed that the germanium dioxide had turned black where it had been in contact with the metal, and that there had been considerable volatilization of this black substance which is most probably germanous oxide. This observation is directly in accord with the statement of Winkler that germanous oxide results when germanium and germanium dioxide are heated together under a layer of borax glass, and contradicts the assertion of

Biltz⁶ that germanium dioxide is not reduced by germanium when a mixture of the two is heated to 1000° in a current of nitrogen.

Since the heat of formation of aluminum oxide is more than twice that of silicon dioxide, and this in turn is undoubtedly greater than that of germanium dioxide, it seemed obvious that germanium might be melted in contact with aluminum oxide without reacting upon it. Consequently a porcelain boat was filled with a paste made by grinding aluminum oxide with a little water, a small bar of wood of the size of the desired ingot was pressed down into this paste and the whole was dried. The piece of wood was then removed and the mould was filled with crystalline germanium. This was melted in nitrogen and a bright bar of the metal was obtained. So far as could be seen, there was no reaction whatever between the germanium and the aluminum oxide. The uneven, upper surface of the bar was smoothed with emery paper and was then used for the determination of the electric resistance and thermoelectric power of the metal.

These determinations were made by Professor C. C. Bidwell of the Department of Physics at Cornell University, and the results appeared in full



in The Physical Review, 19, 447 (1922). They are here shown graphically in Fig. 2. He found that in respect to its electric resistance and thermoelectric power, germanium conforms to its position in the Periodic Table.

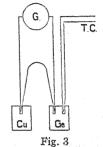
The Molecular Inversion of Germanium.—Bidwell's results cited in the foregoing paragraph show that the thermoelectric power of germanium is a linear function of the temperature, and the resistance is an exponential function of the form, $\log R = \log A + aT + Q/kT$, except in the range 100° to 600°. Between these temperatures there appeared to be a slow, reversible transformation whose completion apparently depended only upon the temperature and not upon the time.

Mr. Hance studied this inversion using the differential method of Roberts-Austen.⁸ This procedure consists in the measurement of the heat effect of the test specimen simultaneously with that of a neutral body.⁹

The general arrangement of the apparatus is shown in Fig. 3. The neutral body was made from a block of pure copper that was obtained

from the United States Mint at Philadelphia. It was cylindrical in shape and of about 2cm. diameter. A hole 4 mm. in diameter was bored into it to half its depth.

Germanium is so brittle that it was impossible to drill holes into it. For this reason it was cast in a special mould in the form of a circular block with 2 holes extending halfway through the block. The weights of the blocks of copper and germanium were made such that the two would have very nearly the same heat capacity. Each block was inserted in a thin-walled graphite shell



which in turn was surrounded by a cylinder of asbestos board. The two were then placed side by side in an alundum electric furnace core of 7.5 cm. bore. In the grooves of this was laid Nichrome wire which was then

covered with refractory cement.

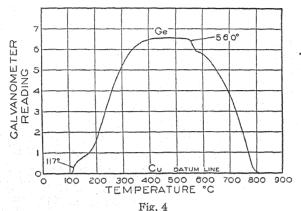
After the wires from the galvanometer G and the thermocouple T.C. were inserted into the openings in the blocks as shown in Fig. 3, the openings and the space around the blocks were tightly packed with asbestos wool. Each block was then covered with a layer of sugar carbon, and the alundum core was next tightly packed to its top with asbestos wool. The cup, thus charged, was placed in a circular box of asbestos board 25cm. wide and 22cm. high, which was then packed with the wool.

After connections with the galvanometer and thermocouple had been made, the heating current was thrown on. The temperature was raised very gradually until 850° was reached, which took about 90 minutes. Readings of the galvanometer deflections and of the temperature of the germanium were made throughout this period at 1-minute intervals. The results are shown in Fig. 4. Inversion began at 117° and reached a maximum at 560°. The experiment was repeated and data concordant with those of the first run were obtained.

⁸ We are greatly indebted to Professor Bidwell for many valuable suggestions during the progress of these determinations.

Hoyt, "Principles of Metallography," McGraw-Hill Book Company, 1920, Part I, pp. 151-156.

It thus appears that germanium passes through a gradual molecular inversion with two or more modifications between the temperatures of 117° and 560° .



Chemical Properties of Germanium

I. Behavior toward Various Gases

Oxygen.—Finely divided amorphous germanium, prepared by the reduction of germanium dioxide in hydrogen, was heated in a porcelain boat in a quartz tube in a current of purified oxygen. The metal was not attacked at 600° even when the temperature was held at this point for 30 minutes. Oxidation began at 605° and proceeded very rapidly at 615° , but was not complete even when the temperature was raised to 900° . The gain in weight at 750° was about 50% of that calculated, and about 90% at 900° . When heated to this latter temperature, the material in the boat was found to be fused to the porcelain and was light gray in color.

These experiments were then repeated with purer germanium that had been fused under sodium sulfate and then finely pulverized. The temperature of the furnace was slowly raised, but no oxidation was observable until the temperature rose to 714° . At this point the powdered metal glowed brightly and white germanium dioxide formed along the edges of the charge and in spots on the top of it. The heating was continued for 30 minutes at 730° and the material was then allowed to cool in oxygen. The product showed a glazed surface and was black in color, with a fine white powder, germanium dioxide, around the edges and distributed irregularly over the top of the mass. The gain in weight of the charge was found to be only 50.8% of that calculated, and the residue in the boat evidently contained germanous and germanic oxides, and metallic germanium. The boat and its contents were then again heated in oxygen, the temperature being gradually raised above 730° . At 900° a white sublimate began to condense in the cool end of the quartz tube. Since germanium dioxide

is not volatile at this temperature, it is evident that the sublimate must be due to the volatilization of germanous oxide which is then further oxidized to the dioxide.

It appears, therefore, to be impossible under the conditions here described, to oxidize germanium quantitatively to the dioxide at a temperature of 730° or lower. At higher temperatures, there is loss of material from the boat through volatilization of germanous oxide.

Hydrogen Sulfide.—Winkler states that when vapor of sulfur is led over germanium that is heated to "incipient redness" (presumably about 600°), the two elements combine to form germanous sulfide, GeS.

Hydrogen sulfide begins to dissociate between 400°10 and 440°.11 To ascertain whether germanium is acted upon by hydrogen sulfide below this dissociation temperature, some of the finely powdered metal was heated in a current of dry hydrogen sulfide at slowly rising temperatures.

No action was apparent up to 290°. At that temperature a slight, yellowish-white deposit appeared in the cool portion of the tube. At 350° this deposit had become heavy. When the temperature dissociation of hydrogen sulfide was reached, the interior of the boat was coated with a yellow deposit and white fumes issued from the tube. At the end of the experiment, 692°, the interior of the tube was so heavily coated with the yellow deposit that the boat was invisible. Minute black crystals were mixed with this yellow coating.

The residue in the boat presented a glazed surface and was of a deep purple color, which persisted when the material was powdered. There was copious evolution of hydrogen sulfide when the material was treated with coned. hydrochloric acid.

The results of the experiment indicate that germanium is not attacked by hydrogen sulfide at temperatures below 200°, and that the action of the gas upon the metal is comparatively slight until dissociation of the hydrogen sulfide begins, when the reaction becomes that between sulfur and germanium with the formation of germanous sulfide as noted by Winkler.

Sulfur Dioxide.—Finely pulverized germanium was heated in a current of sulfur dioxide which had been dried and freed from sulfur trioxide by passing it through concd. sulfuric acid. The temperature was gradually raised to 672° .

When cool, the boat was withdrawn and examined. Its contents were yellowish-gray in appearance, and the end of the boat which was farthest from the sulfur dioxide inlet was covered with a heavy coating of a fine white powder. The cool end of the quartz tube was also coated with a heavy white deposit. When heated with hydrochloric acid, both the white powder and the yellowish-gray material in the boat gave off hydrogen sulfide.

¹⁰ Myers, Ann., 159, 124 (1871).

¹¹ Pelabon, Compt. rend., 124, 35, 686 (1897).

The results show that sulfur dioxide acts upon crystalline germanium at a temperature somewhat below 500°, that this action is rapid between 510° and 530°, and that the disulfide and the dioxide of germanium are formed in the reaction.

II. Behavior in Various Liquid Reagents

Small weighed pieces of fused germanium were immersed in the reagents listed below. They were allowed to stand at room temperature for 1 week, and were then removed, washed with distilled water, dried at 110° and weighed.

Weighed samples were then placed in the same reagents which were maintained at a temperature of 90° for 8 hours. The samples were again washed, dried and weighed.

At room temperature and at 90°, water, a 50% solution of sodium hydroxide, 1:1 hydrochloric acid, concd. hydrochloric acid or 1:1 sulfuric acid did not act upon the metal, which remained bright and lost no weight. The germanium was slightly tarnished by a 10% solution of sodium hydroxide, both cold and warm, and lost about 0.5% in weight. Dilute nitric acid, 1:1, acted upon the metal superficially with the formation of white germanium dioxide, and the loss in weight amounted to about 7% at room temperature and 1.6% at 90° . Concd. nitric acid darkened the surface of the metal, but there was no appreciable loss in weight. The metal was not attacked by concd. sulfuric acid at room temperature, but lost 1% in weight at 90° . Hydrofluoric acid, 19N, caused a loss in weight of only 0.1% at room temperature, and about 0.8% at 90° . Immersion in a 3% solution of hydrogen peroxide at room temperature for 1 week resulted in a loss of weight of about 40%, and at 90° for 8 hours the loss in weight was about 70%.

When finely powdered germanium is digested in a 3% solution of hydrogen peroxide at about 100°, it finally dissolves entirely and the product, germanium dioxide, dissolves in the water present. This solubility of germanium in hydrogen peroxide, which was first observed by us early in 1921, appears to offer an excellent method for determining the atomic weight of germanium by means of the ratio Ge: GeO₂. This will be studied in the near future in this Laboratory.

III. Behavior of Germanium when Fused with Various Solid Reagents

Potassium Hydroxide.—Ten g. of potassium hydroxide was melted in a nickel crucible and was heated until water had been expelled. A small piece of fused germanium weighing 0.0992 g. was then dropped into the molten mass. It began to dissolve immediately with the copious evolution of tiny bubbles. The mass was kept molten and in 10 minutes the reaction ceased and the metal had entirely disappeared. When dissolved in water, the material gave a clear, colorless solution.

Sodium Hydroxide.—The reaction was similar to that with potassium hydroxide.

Potassium Hydrogen Sulfate.—A small particle of germanium weighing $0.1534~\rm g$. was dropped into a platinum crucible containing $10~\rm g$. of molten potassium hydrogen sulfate and allowed to remain there for $10~\rm minutes$. No visible reaction occurred. The sample, however, lost 6% in weight, showing that the metal is slowly attacked by this reagent.

Sodium Carbonate.—Fragments of crystalline germanium were dropped into molten sodium carbonate. The metal was rapidly attacked, with the evolution of gas and with the projection of bright sparks from the surface of the reagent. The metal was eventually dissolved.

Potassium Cyanide.—Molten potassium cyanide was without action. Potassium Chlorate.—Molten potassium chlorate very slowly attacked germanium, and at the end of 30 minutes a small amount of metal had passed into the solution.

Potassium Nitrate.—When small pieces of germanium were dropped into the molten potassium nitrate, there was immediate reduction of the nitrate and evolution of gas. The germanium was oxidized and was found to be present in the water solution of the residue.

Sodium Peroxide.—The reagent was carefully melted and a small amount of germanium was dropped into it. Vigorous reaction at once took place and continued until the germanium had entirely passed into solution.

Germanium Carbide

Preliminary experiments upon the formation of a carbide of germanium analogous to silicon carbide, SiC, led to negative results. When a mixture of finely powdered germanium and sugar carbon was heated in a small electric furnace, part of the germanium vaporized and burned in the air, and part of it condensed on the upper portion of the crucible as brown germanous oxide. The germanium that remained in the crucible was found to have fused into globules, but there was no evidence of combination of the metal with carbon. The experiments will be continued.

Summary

This article deals with the dehydration of germanium dioxide, the reduction of germanium dioxide by aluminum and by hydrogen, the preparation of fused germanium, the behavior of germanium when heated in hydrogen, the melting point, specific gravity, hardness, crystal form, electric resistance, thermoelectric power, molecular inversion and sprouting of germanium, and the behavior of the metal toward various gases, liquid reagents and molten solid reagents.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN A BROMINE-BROMIDE SOLUTION. II. RATE MEASURE-MENTS IN DILUTE SOLUTIONS AND IN THE ABSENCE OF SULFATE, AND THEIR INTERPRETATION AS A FUNCTION OF THE ACTIVITY PRODUCT OF HYDROBROMIC ACID

By Robert S. Livingston and William C. Bray Received June 5, 1923

Introduction

In a previous paper on the catalytic decomposition of hydrogen peroxide in a bromine-bromide solution, a series of rate measurements were given for the steady-state condition, and the following kinetic equation was determined.

$$-d(H_2O_2)/dt = K(H_2O_2) (H^+) (Br^-)$$
 (1)

where K is approximately equal to 0.0144 for acid concentrations between $0.2\ N$ and $3.0\ N$. The concentrations used were expressed in moles per liter, and were computed on the assumption that all the electrolytes were completely ionized. It was pointed out at that time that the value of K, obtained from measurements in solutions of potassium bromide and sulfuric acid, increased as the acid concentration was decreased below $0.2\ N$. To determine the nature of this effect, steady-state rate measurements have now been made in still more dilute solutions of sulfuric acid and potassium bromide, and in various acid-bromide solutions that do not contain sulfate.

Experimental Measurements

As before, the reactions were conducted at 25° in the dark. The experimental conditions, methods, and method of computing used were the same as those explained in detail in the earlier paper.

At low acid concentration the decomposition of hydrogen peroxide in the absence of the catalyst introduces a fairly important error. To determine what concentration of acid was necessary to render this effect negligible, three blank solutions were prepared. Each blank contained 0.12 M hydrogen peroxide. To two of them sulfuric acid was added to make them 0.0098 N and 0.073 N, respectively. The first order constant (k) for the neutral solution was 0.176×10^{-4} , a more rapid rate than that at 0.0147 N acid, Expt. 7, Table I. No appreciable loss occurred during a 3-day

¹ Bray and Livingston, This Journal, **45**, 1251 (1923). On p. 1253, fifth from the last line, F_{298} ° is a misprint for ΔF_{298} °.

Recently our attention has been called to a paper by Trifonow: "Eigenschaften und Struktur der Persalpetersäure" (Trifonow, Z. anorg. Chem., 124, 123 (1922)). He mentions the oxidation of bromide and the reduction of bromine by hydrogen peroxide, and states that the former reaction may be retarded by dilution and the latter by the addition of a fairly large quantity of KBr and $\rm H_2SO_4$.

period, in either of the acidified solutions, although these experiments were made in ordinary glass containers. To reduce this effect, wax-lined bottles were used in several of the experiments conducted at low acid concentration (Expts. 7, 8 and 9 of Table II, and 3 and 6, of Table VI).

Steady-State Measurements in the Presence of Dilute Sulfuric Acid

The results of 7 determinations of the steady-state rate in the presence of dil. sulfuric acid are summarized in Table I. The arrangement and conventions adopted are the same as those used in the third table in the preceding paper. In this table (I) the peroxide concentrations marked with an asterisk were made up from "Superoxol," the others from a 3% commercial solution. Since the interest of this table is primarily in the rate constants, the values of "bromine-calculated" and "tribromide-calculated" have been omitted; the "calculated" bromine concentrations were used, however, in computing the values of R listed. The last three columns will be explained later.

Table I
Steady-State Rate Measurements in the Presence of Dilute Sulfuric Acid

	Initial o	onon	Stea	dy-state co Bromide	nen.			
Expt.	Acid	Bromide	Acid	meas.	Bromine	Peroxide	$k \times 10^4$	R
1	0.0976	0.0982	0.0973.	0.0979	0.00014	0.03-0.01	* 1.80	0.59
2	.0835	.070	.0835	.070	.000028	.0905	1.22	.26
3	.0645	.100	.0644	.100	. 000053	.1608	1.30	.49
4	.0465	.0935	.0465	.0935		.0201	* 0.937	
5	.0257	.103	.0257	. 103		.0301	* .615	
6	.01965	.0342	.01965	.0342	4	.2118	* .1826	• •
7	.01473	.0244	.01473	.0244		.2119	.1081	• •
	Expt.	K		μ	γ		x	
	1	0.018	39	0.244	0.7	74 (0.0315	
	2	.020	08	. 195	.7	84	.0335	
	3	.020)2	.197	.7	84	.0325	
	4	.02	16	.164	.7	92	.0344	
	5	.023	32	. 142	.7	98	.0364	
	6	.027	72	.0537	.8	27	.0398	
	7	. 030	01	.0465	.8	54	.0413	

The value of K is seen to increase as the acid concentration is decreased. It is apparently approaching a limiting finite value, and is not increasing indefinitely, as it would if there were any appreciable catalysis in a neutral bromide solution. To demonstrate this, the ratio of the first order constant to the bromide concentration, $k/(Br^-)$, has been plotted against the hydrogen-ion concentration, (H^+) , Fig. 1. Results from Table III of the first paper, as well as those from Table I, are represented. It is apparent that when this curve is extrapolated to $(H^+) = 0$ (practically identical with neutral solution on this scale) it will pass through or very near the origin; that is, the absolute rate of the catalytic decomposition will be

following form:2

negligibly small. Since the rate of the reaction between bromine and peroxide is very rapid in neutral solution, it follows that the rate of oxidation of bromide by peroxide is negligible under these conditions, for any bromine formed by this reaction would be rapidly reduced with the resultant decomposition of hydrogen peroxide. This is in marked

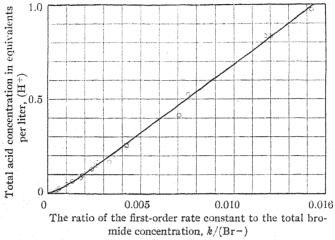


Fig. 1

contrast to the iodide-peroxide reaction, the rate equation for which has the

$$d(I_2)/dt = (I^-) (H_2O_2) [K' + K(H^+)]$$
 (2)

Our results demonstrate that the constant term (K') is unnecessary in the rate equation of the bromide oxidation.

Since the possibility of an independent reaction not involving acid has been eliminated, the most plausible explanation of the increase of K with a decrease in acid concentration is the assumption that the sulfuric acid is not completely ionized. It will be recalled that all values of K and R were computed upon the assumption that sulfuric acid was completely ionized. The assumption of incomplete ionization is in agreement with a series of measurements by Noyes and Stewart,³ who state that singly-ionized sulfuric acid (HSO₄⁻) may be considered as a weak acid, with an ionization constant of 3×10^{-2} in the range $0.1\,M$ to $0.025\,M$ sulfuric acid. It should also be noted that when sulfuric acid is treated as a strong electrolyte the values of the activity coefficients for dilute solutions are very low.

Steady-State Measurements in Hydrobromic Acid Solutions

To discover to what extent the observed increase of the constant in dilute solution was due to the presence of sulfuric acid, a series of steady-state

- ² Bray, Z. physik. Chem., 54, 486 (1906).
- Noyes and Stewart, This Journal, 32, 1133 (1910).
- ⁴ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 357.

rate measurements were made in which the only electrolyte was hydrobromic acid. The results of 9 such measurements are summarized in Table II. In all the experiments listed the initial peroxide concentrations were made up to $0.16\,M$ or greater, from a "Superoxol" solution.

Table II
Steady-State Rate Measurements in Hydrobromic Acid Solution

	Initial conen.	Stea	dy-state c	oncn. Bromine						
Expt		Acid	Bromide		$6 imes 10^4$	K	R	μ	γ	x
1	0.429	0.346	0.311	0.0417	26:8	0.0250	0.60	0.346		
2	.286	.256	.244	.0150	17.0	.0271	.76	.256		
3	.214	.206	.203	.0042	11.2	.0268	. 57	. 206	0.782	0.0438
4	.147	.146	.146	.00051	5.96	.0279	. 33	.146	.796	.0440
- 5	.0945	.0945	.0945		2.58	.0289		.0945	.817	.0433
6	.0677	.0677	,0677		1.36	.0297		.0677	.834	.0427
7	.0432	.0432	.0432		0.593	.0318		.0432	.858	.0432
8	.0338	.0338	.0338		0.384	.0337		.0338	.870	.0445
9	.0217	.0217	.0217		0.164	.0348		.0217	.889	.0440

The average value of K obtained from these measurements is about twice as great as the average value (0.0144) obtained in sulfuric acid solutions above $0.2\ N$, but is only slightly greater than the average value obtained from measurements in dil. sulfuric acid solution, Table I. Below $0.3\ N$ acid the value of K increases regularly as the hydrobromic acid concentration is decreased. At higher concentrations, for which the rate is very rapid, the values obtained for K were not always concordant and there is some evidence for the existence of a small amount of bromate at the steady state.

Two additional experiments were performed to discover what factor was responsible for the low rates observed in the sulfuric acid-potassium bromide solutions.

Expt.	Initial HBr	conens. Na ₂ SO ₄		Steady-sta Bromide	te conens. Acid	R	K
A	0.1881 M	0.492 M =	= 0.964 N	$0.1880 \ M$	0.1880 N	0.0080	0.0042
		H_2SO_4					
В	.113~M	.976 N		.100~M	1.08 N	.445	.0239

These experiments show that the effect is due to the sulfate ion. Taken in conjunction with the results with solutions of sulfuric acid and potassium bromide and with hydrobromic acid solutions, they show that the value of K increases towards a definite value when the ratio, $\Sigma SO_4/\Sigma$ acid, is decreased without limit, and that it decreases indefinitely when the ratio is increased. The approximate constancy of K in the third table of the preceding paper was due to the constant ratio of sulfate to acid, and therefore the average value of the constant (0.0144) is not fundamental.

The values of R, $(Br_2)/(H^+)^2$ $(Br^-)^2$ vary with the ratio of sulfate to acid in the same direction but more rapidly than the values of K, as is shown in Table III.

Table III
THE Specific Effect of the Sulfate Ion

Expt.	$\Sigma SO_4/\Sigma_{acid}$	K	R
A	2.6	0.0042	0.008
Av. of Table III, Ref. 1		.0144	. 22
B	45	.0239	.45
Av. of Table II		.03	.60

It is evident that these results are in agreement with the assumption that singly-ionized sulfuric acid is a weak acid.

The Rate of Appearance of Bromine in Hydrobromic Acid Solution

As an additional check on the mechanism,⁵ an experiment was performed on the rate of appearance of bromine in hydrobromic acid solution. The results were computed by the second method, explained in the preceding paper.⁶ The smoothed out data and computations are given in Table IV.

TABLE IV

RATE OF	APPEARANC	E OF BROMI	NE IN A	Hypro	BROMIC	ACID So	LUTION
$t-l_0$	c	oncentrations			Rates	\times 104	
Min.	Bromine	Peroxide	HBr -	$d(H_2O_2)/c$	$lt d(Br_2)/$	dt Sum.	$2K_1$
0	0	0.0292	0.294				
5	0.00020	.0290	.294	4.0	3.4	7.4	0.029
10	.00038	.0288	.293	4.0	3.1	7.1	.029
20	.00069	.0284	.293	4.0	2.8	6.8	.028
30	.00099	.0280	.292	4.0	$^{2.4}$	6.4	.027
40	.00122	.0276	.292	4.0	2.4	6.4	.027
60	.00170	.0268	.291	3.8	2.2	6.0	.026
80	.00216	.0261	.290	3.6	1.8	5.4	.025
100	00233	-0254	289	3.1	1.6	4.8	.023

The average value of $2 K_1$ is 0.0273. This is in excellent agreement with the value of K (0.0271) obtained from steady-state measurements, with an initial hydrobromic-acid concentration of 0.286 M. It is not known whether the observed small decrease of $2 K_1$ with time has any theoretical significance or is due to experimental error.

Steady-State Measurements in Solutions of Perchloric and Hydrobromic Acids

Since perchloric acid is a strong non-reactive acid, it was chosen as a substitute for sulfuric acid. A series of experiments, which were performed in relatively dilute solutions containing perchloric and hydrobromic acids, are summarized in Table V.

In only three of these experiments was the bromine concentration measurable; $0.00089\,M$ in 1, $0.000016\,M$ in 2, and $0.00008\,M$ in 5. The corresponding values of R are $0.35, 0.43\,\text{and}\,0.27$, respectively. The values of K obtained are of the same order of magnitude as those obtained in pure hy-

⁵ Ref. 1, pp. 1261, 1270,

⁶ Ref. 1, p. 1266.

drobromic acid solution, and like the latter, they increase as the concentration of electrolyte is decreased.

Table V

Steady-State Rate Measurements in Solutions Containing Perchloric Acid

		conen.		dy-state co					
Expt.	$HC1O_4$	$_{ m HBr}$	Acid	Bromide	$k \times 10^4$	K	μ	γ	×
1	0.370	0.0719	0.4405	0.0766	7.52	0.0223	0.442		
2	.2778	.0180	.2958	.0180	1.353	.0254	. 296		
3	.222	.0144	.236	.0144	8.94	.0262	.236	0.775	0.0436
4	.148	.0540	.202	.0539	2.91	.0267	.202	.782	.0432
5	.185	.0144	.199	.0144	0.752	.0267	.199	.783	.0426
6	.0924	.0720	.164	.0719	3.18	.0269	. 164	.792	.0429
7	.0924	.0288	.121	.0288	1.00	.0287	.121	.805	.0443
8	.0462	.0540	.100	.0540	1.59	.0293	.100	.814	.0442
9	.0370	.0144	.0514	.0144	0.240	.0324	.0514	. 849	.0449

The Steady State in Solutions Containing Metallic Bromides

Several experiments were performed in solutions containing barium or potassium bromide. The results of these experiments are summarized in Table VI.

TABLE VI

STEADY-STATE RATE MEASUREMENTS IN SOLUTIONS CONTAINING METALLIC BROMIDES

	T-147-1		Stea	dy-state c							
No.	Initial o HBr	KBr	Acid	Bromide	Bromine meas. k	\times 104	K	R	μ	γ	x
1	0.113	0.196	0.107	0.306	0.00286	7.83	0.0239	0.45	0.306		
2	.0540	.1464	.0537	.2001	.00014	2.854	.0264	.28	.200	0.782	0.0430
3	.0719	.0732	.0716	.1448	.00013	2.880	.0278	.36	. 145	.797	.0437
4	.0360	.0732	.0359	.1090	.000024	1.123	.0286	. 54	. 109	.810	.0435
5	.0134	.0736	.0134	.0870		0.378	.0322		.0870	.821	.0477
6	.0268	.0245	.0268	.0514		.459	.0333		.0514	.837	.0475
7	.0216	0146	.0216	.0363		.277	.0352		.0363	.868	.0469
	HBr	1/2BaBr	2								
8	.0719	.0528	.0717	.1245	.000094	2.44	.0272	.39	.151	.795	.0431
9	.0540	.0264	.0540	.0804		1.30	.0299		.0936	.817	.0447
10	.0176	.0176	.0360	.0352		0.613	.0318		.0624	.838	.0453
	HC1O ₄	KBr									
11	.0924	.0491	.0924	.0491		1.29	.0283		.141	.798	.0445
12	.0462	.0491	.0462	.0491		0.688	.0294		.0953	.816	.0442

The values of K obtained from measurements in these solutions have the same magnitude and trend as those obtained in hydrobromic acid solutions.

Theoretical Discussion

Substitution of Activities for Concentrations in the Rate Equation

The gradual increase in the specific reaction rate with a decrease in the concentration of the catalyst, 7 at low concentrations, suggests that activi-

⁷ For convenience, the term catalyst has been used to refer to that unit of the catalytic pair, the concentration of which occurs in the steady-state rate equation, in this case hydrobromic acid.

It should be noted that it is not illogical to use steady-state data in determining the effect of activities upon rates. In the present case the steady-state rate (rate of decomposition of peroxide) is exactly twice the rate of Reaction 1 (oxidation of bromide), and the two-rate equations differ only by a factor of 2 in the constant.

ties rather than concentrations should be used in the rate equation. Recently several cases of catalytic-rate measurements have been reported for which fairly accurate constants could be obtained by substituting activities for the concentrations of the reacting ions, in the rate equations. Fales and Morrell⁸ applied this correction to the acid hydrolysis of cane sugar. Harned and Pfanstiel⁹ have used a similar method in studying the acid hydrolysis of ethyl acetate. In both cases the use of activities improved the constancy of the specific reaction rate, but still left much to be desired. A more satisfactory example is the rearrangement of acetylchloro-aminobenzene to p-chloro-acetanilide in the presence of hydrochloric acid, which was investigated by Harned and Seltz.¹⁰ This case differs from the other two cited in that it involves the activity of hydrochloric acid rather than the individual ion activity of hydrogen ion.

The reaction discussed here, like the rearrangement of acetyl-chloroaminobenzene, involves the activity of the halide acid, and not the activity of any individual ion. Assuming that the rate is determined by the product of the activities of the ions of the catalyst, and the concentration of the non-electrolyte (hydrogen peroxide), the rate may be expressed by the following equation.

$$-d(H_2O_2)/dt = \chi(H_2O_2)a_H + a_{Br} = \chi(H_2O_2) (H^+) (Br^-)\gamma^2_{HBr}$$
(3)

It follows from Equation 1 that the relation of the "activity-rate" constant (x) to the "concentration-rate" constant (K) is given by the following expression.

$$K/\gamma^2_{\rm HBr} = \chi \tag{4}$$

Data on the activity of hydrobromic acid solutions are rather meager, but the electromotive-force measurements of Storch¹¹ tend to show that below $0.10\ N$ the activities of hydrobromic and hydrochloric acids are identical.¹²

To correlate the observations in the various solutions used, which involved mixed electrolytes of various valence types, it is necessary to introduce the concept of ionic strength.¹³ Since it has been demonstrated empirically that, in dilute solutions, the activity of a solute is a function of the total ionic strength and is independent of the nature of the other solutes,

- ⁸ Fales and Morrell, This Journal, 44, 2072 (1921).
- 9 Harned and Pfanstiel, ibid., 44, 2193 (1922).
- 10 Harned and Seltz, ibid., 44, 1480 (1922).
- 11 Lewis and Storch, ibid., 39, 2544 (1917).
- 12 Ref. 4; pp. 335, 336.
- 13 The ionic strength may be defined as half the sum of the products of the stoichiometrical molalities of the ions and the squares of their valences. Thus, for sulfuric acid the ionic strength is 3 times the molal concentration. Compare Ref. 4, p. 373. In the present paper the concentrations in moles per liter have been used instead of molalities, but the resulting numerical difference is not appreciable except in the more concentrated solutions.

we may assume that in the various mixed solutions used the activity coefficient of hydrobromic acid, $\gamma_{\rm HBr}$, is a function of the ionic strength, μ , only.

In the last columns of Tables I, II, IV and V, the values of the ionic strength, μ , the mean activity coefficient, $\gamma_{\rm HBr}$, and the rate constant corrected for the activity effect, χ , are listed. Values of the corrected constant have been computed for ionic strengths below 0.25, although it is hardly to be expected that either the assumption of the identity of the activities of hydrobromic and hydrochloric acids or the ionic-strength principle can be applied over this entire range. With the exception of the measurements in sulfuric acid solutions in Table I, the values of the corrected constants (χ) do not show any marked trend. The average value for pure hydrobromic acid solutions (Table II) is 0.0437 ± 0.0005 . For perchloric-hydrobromic acid solutions (Table IV) the average value is 0.0437 ± 0.0006 . On the other hand, the uncorrected constant (K) for the same experiments varies from 0.0348 to 0.0260, a decrease of 25.3%.

Taking 0.0437 as the average value of χ , values of K for a series of ionic strengths may be computed by Equation 4, from the values of γ_{HCI} given by Lewis and Randall.¹² Table VII lists the values so obtained.

Table VII
The Calculation of K from x=0.0437 and γ

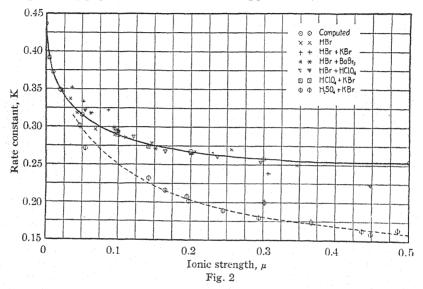
μ	γ _{HCI}	K(Computed)	μ	γ _{HCl}	K(Computed)
0	1,000	(0.0437)	0.100	0.814	0.0289
0.005	0.947	.0392	.200	.783	.0268
.010	.924	.0373	.300	.768	.0258
.020	.894	.0349	.500	.762	.0254
.050	(.850)	.0316			

In Fig. 2, K (computed) has been plotted against μ . The experimental values of K, Tables I, II, V and VI and the first 6 values of Table III (Ref. 1), have also been plotted. At ionic strengths below 0.25, the values of K obtained in pure hydrobromic acid solutions and in perchloric-hydrobromic acid solutions are in remarkable agreement with the theoretical curve.

Although rate measurements cannot be used very generally for the determination of activity coefficients, they may be useful in certain limited cases. The data presented here have been used to obtain an estimate of the activity of hydrobromic acid, in solutions containing various electrolytes, relative to its activity in pure aqueous solutions. The results of such considerations are summarized as follows.

1. The activity of hydrobromic acid in perchloric acid solutions (less than 0.25μ) is almost identical with that of pure hydrobromic acid solutions of the same ionic strength. At higher concentrations there is apparently a small negative departure.

- 2. In all solutions containing metallic bromides the activity seems to be slightly greater below 0.15μ and slightly less above 0.15μ than the activity in pure hydrobromic acid solutions of the same ionic strength.
- 3. If it be assumed, and it is not an improbable assumption, that the presence of sulfuric acid does not depress the specific rate of the catalyzed decomposition, we may use the data given in Table I and in Table III of the preceding paper (Ref. 1) to obtain an approximate estimate of the ac-



tivity coefficient of hydrobromic acid in potassium bromide-sulfuric acid solutions over a wide range of concentrations. The activity coefficient so obtained is practically independent of variations in the ratio (KBr)/(H₂-SO₄) from 2.0 to 0.035. A few averaged values are given in the following table.

TABLE VIII

THE ACTIVITY COEFFICIENT OF HYDROBROMIC ACID IN SOLUTIONS OF SULFURIC ACID AND POTASSIUM BROMIDE

Although the general idea, that activities or "active mass" should be substituted for concentrations in the rate equations, has been discussed for years, one of the first attempts at an experimental test of this principle was made by Bugarsky¹⁴ in 1910. He measured the rate of reaction between alcohol and bromine in 4 different solvents and attempted to estimate the activities by means of partition coefficients. In 1920, Jones and W. C. McC. Lewis¹⁵

¹⁴ Bugarsky, Z. physik. Chem., 71, 705 (1910).

¹⁵ Jones and W. C. McC. Lewis, J. Chem. Soc., 117, 1123 (1920).

studied the acid hydrolysis of sucrose. They obtained their hydrogen-ion activities from cell measurements in the presence of the sugar, but their results are rendered somewhat uncertain by the presence of a diffusion boundary in their cell. This is also true for the results of Fales and Morrell.⁸ The type of equation, used by Jones and Lewis¹⁵ and the more recent workers^{8,8,10} is one in which activities are substituted for the corresponding concentration terms. Following this convention, the rate equation for the bromine-bromide catalysis would be

$$-d(H_2O_2)/dt = K'a_{H_2O_2}a_{H} + a_{Br} - K'(H_2O_2) (H^+) (Br^-)\gamma_{H_2O_2} \gamma^2_{HBr}$$
 (5)

To bring this equation into agreement with the experimental data it is necessary to assume that $\gamma_{\rm H_2O_2}$ is constant in electrolyte solutions whose ionic strengths vary from 0.25 to 0.02. Although there is no definite evidence on this point, it seems an improbable assumption.

Recently Brönsted¹⁶ has pointed out that the substitution of activities for concentrations in rate equations cannot be generally used to obviate "reaction anomalies," for in dilute solutions the activity coefficients of all electrolytes decrease as the total electrolyte concentration is increased, while under these same conditions the rate constants decrease, increase, or are unaffected by a change in the electrolyte concentration. He assumes that all reactions proceed through the formation and decomposition of an unstable intermediate, the valence of which is the algebraic sum of the valences of its components. From these assumptions he shows that it is consistent with thermodynamics and in good agreement with experimental results to represent the rate of any actual reaction as proportional to the product of the activities of the component molecular species divided by the activity coefficient of the intermediate complex. In agreement with this system the law of the bromine-bromide catalysis would be

$$-d(H_2O_2)/dt = \frac{K''}{\gamma_{H_2O_2 \cdot HBr}} a_{H_2O_2} a_{H^+} a_{Br^-} = K''(H_2O_2)(H^+)(Br^-)\gamma^2_{HBr} \frac{\gamma_{H_2O_2}}{\gamma_{H_2O_2 \cdot HBr}}$$
(6)

In order that this equation shall represent the experimental data it is necessary for the ratio of the activity coefficients of hydrogen peroxide and the neutral complex (H₂O₂.HBr) to be constant over the range of concentrations studied. There is no reason to believe this assumption improbable.

The evidence presented here, as well as that presented by Harned and Seltz, ¹⁰ demonstrates that the rate of a catalytic process involving neutral molecules is proportional to a function of the activity of the catalyst rather than of the concentration. If the activity coefficient of the substance undergoing transformation is constant, as Harned assumes, the facts may be expressed equally well by the "activity-rate" theory or by Brönsted's theory. ¹⁷ If this assumption proves to be false, these results may be taken

¹⁶ Brönsted, Z. physik. Chem., 102, 169 (1922).

¹⁷ For a discussion of these theories and additional references, see the paper by Scatchard, This Journal, 45, 1580 (1923), which appeared while this article was in proof.

as a definite confirmation of a special case of Brönsted's theory. We shall continue this investigation by direct measurement of the activities involved and by further rate measurements.

Summary

- 1. The steady-state rate of the bromine-bromide catalysis of hydrogen peroxide has been measured in dil. solutions of sulfuric acid and potassium bromide, and it has been shown that the rate constant approaches a definite finite value as the sulfuric acid is indefinitely decreased.
- 2. The steady-state rate has also been measured in the following solutions: hydrobromic acid, hydrobromic-perchloric acid, hydrobromic acid-potassium bromide, hydrobromic acid-barium bromide, and perchloric acid-potassium bromide. The rate constants obtained from measurements in these various solutions are all slightly larger than those obtained from measurements in dil. sulfuric acid solutions, and are about twice as great as those obtained in sulfuric acid solutions above $0.2\,N$.
- 3. At the steady state, in hydrobromic acid and hydrobromic-perchloric acid solutions of ionic strength less than 0.25 and in 8 out of the 12 remaining experiments in the absence of sulfate, the rate of decomposition of peroxide is represented by the following expression within the limits of experimental error, 1% to 2% (the discrepancy in the 4 excepted experiments lies between 4% and 9%):

$$-d(H_2O_2)/dt = 0.0437 (H_2O_2) (H^+) (Br^-)\gamma^2_{HBr}$$
 (7)

- 4. The activity coefficient of hydrobromic acid in solutions containing sulfuric acid and potassium bromide has been estimated from the rate measurements in these solutions, by the assumption that Equation 7 holds.
- 5. The application of the "activity-rate" theory and of Brönsted's theory to the experiments presented here has been briefly discussed.

BERKELEY, CALIFORNIA

[Contribution from the Chemical and Physical Laboratories of the University of Missouri]

LUMINESCENCE OF ORGANO-MAGNESIUM HALIDES

By R. T. Dufford, S. Calvert and Dorothy Nightingale Received June 7, 1923

Apparently the first notice of luminescence associated with a Grignard reagent dates from 1906, when Wedekind¹ found that phenylmagnesium bromide and phenylmagnesium iodide give a bright light when reacting with chloropicrin. This reaction has become widely known as the "Wedekind Reaction."

¹ Wedekind, Ber., 4, 417 (1906); Physik. Z., 7, 805 (1906); Chem. Zentr., 30, 921 (1906); Z. wiss. Phot., 5, 29 (1907).

Heczko,² in repeating the experiment, noticed that these compounds are luminous when oxidized in air. He thought moisture necessary to produce the light, but this idea was shown to be wrong by Moeller; in fact, tests by the writers have shown definitely that the presence of moisture tends to inhibit the light. Other workers occasionally have noted, incidental to synthetic work, that certain Grignard compounds give light. Thus, Schmidlin³ reports light from diphenylmagnesium bromide, but wrongly reports several other compounds to be non-luminous. Späth⁴ mentions p-chlorophenylmagnesium bromide and m-p-xylylmagnesium bromide as brightly luminescent. These are isolated references that came to the attention of the writers only after most of their work had been done.

Moeller,⁵ in 1914, reported a systematic investigation of 10 such compounds. The original Danish article is practically unavailable in this country, and it has not been adequately abstracted. The growing interest in these compounds makes it seem desirable to give here a summary of his results, although several of his statements have been shown by later workers to be incorrect. The writers, on finally obtaining a photostatic copy of the article, found that they had already rediscovered all but one of the compounds mentioned, and would have recorded their results on that one also within a few days more. It is hoped that others will be saved this experience. The results reported by Moeller are as follows.

"Good"	"Weak"	"No read	ction"
C ₃ H ₇ MgBr (wrong)	C ₂ H ₅ MgBr (wrong)	C ₃ H ₇ Cl)	
C ₆ H ₅ MgBr	C ₅ H ₁₁ MgBr (wrong)	C ₅ H ₁₁ Cl	435
p-BrC ₆ H ₄ MgBr	C ₆ H ₅ MgI	C ₆ H ₅ Cl	and Mg
α -C ₁₀ H ₇ MgBr	C ₆ H ₅ CH ₂ MgBr (wrong)	C ₆ H ₃ Br ₃	
α - α - $C_{10}H_6Br_2$ and Mg			
b-CH-C-H-MgBr			

Moeller also pointed out that oxygen, not moisture, is needed to produce luminescence.

An attack on the problem from quite another angle was made by Lifschitz, whose early work seemed to indicate that differences in the stabilities of the etherates might account for the difference in behavior between aliphatic and aromatic Grignard compound in ether solution. Later work showed that the differences were less than at first was supposed, and that his original explanation was inadequate. The work is, nevertheless, an exceedingly valuable contribution to the chemistry of these compounds. A connection with unsaturation is suggested.

The luminescence of $p\text{-Br}C_6H_4MgBr$ was independently discovered by W. V. Evans, and investigated with one of the writers, who pointed out also that an interesting fluorescence is shown by the product of oxidation of this compound, and that the fluorescence and the chemiluminescence are not identical. The oxidation of $p\text{-}C_6H_4MgBr$ gives about as much light as any of the older classical chemiluminescent reactions. The writers suggest the name "Moeller-Evans Reaction" for it in honor of the discoverers. It has been used frequently in the present work for comparison with other reactions, and the name will be convenient for reference. In the course of this work, all the classical chemiluminescent reactions were repeated for comparison.

² Heczko, Chem. Zentr., 35, 199 (1911).

³ Schmidlin, Ber., 45, 3172 (1912).

⁴ Späth, Monatsh., 36, 4 (1915).

⁵ S. Moeller, Arch. Pharm. Chem., 21, 449, 466 (1914).

⁶ Lifschitz, Helietica Chim. Acta, 1, 482 (1918).

⁷ Lifschitz and Kalberer, Z. physik. Chem., 102, 393 (1922).

⁸ Evans and Dufford, This Journal, 45, 278 (1923).

An extensive examination of over 60 Grignard compounds has been carried out by the present writers, in which more than 40 luminous compounds have been studied. The effects on the color and the brightness of the chemical nature of have been determined for several factors, such as the chemical nature of the reacting atoms, the position, the mass and the chemical nature of substituents, unsaturation and molecular structure. Certain fluorescent effects have been noted, also. We shall discuss first the chemiluminescence in ether solution on oxidation with oxygen.

Experimental Methods

Where possible, the compounds used were purchased from a commercial source. The majority of the aromatic halogen bodies were synthesized in the Organic Laboratory of the University of Missouri, from materials so purchased. The methods of synthesis chosen were those which seemed calculated to yield the purest products, and in these cases, the products were tested carefully. The results, it is believed, are therefore entitled to confidence in this respect.

In preparing the Grignard reagents, in most cases the attempt was made to use equivalent quantities of material, so that the results would be as nearly comparable as possible with such unstable compounds. With certain of the less soluble compounds it was necessary to work at greater dilutions than usual. The concentrations used were near the optimum.

For studying the spectral distribution of light, the Weiser¹⁰ method of color filters was used, much as in the preliminary work by Evans and Dufford, but with a slightly improved set of filters, as described in Table I. The photographic method is unreliable at the red end of the spectrum and was, therefore, supplemented by visual observations through a second set of filters. The photographs are more reliable than the eye at the violet end of the spectrum, however. For accuracy, both methods are necessary.

Table I Transmissions of Monochromatic Filters

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Window Mfr's. No. No.	Color	Approximate Wave length of spectral range max, transmission	
1 α	red	limit of visible to λ 6450 λ 6690	
2 γ	orange	λ 6450-5800 with faint band	
		λ 7300–6700 λ 6050	
3 δ	yellow-green	λ 6250-5500 with faint band	
		λ 7330-6760 λ 5830	
4 €	green	λ 5700-5100 λ 5340	
5 η	blue	λ 5400-4600 λ 4870	
6 ₽	violet	λ 4800-4100, and faintly to λ 3500 λ 4550	
7 G586A	ultraviolet	λ 4200–3000 λ 3600	

⁹ Dufford, Calvert and Nightingale, Phys. Rev., 21, 203 (1923), (abstract); a paper on this work was read at the New Haven Meeting of The American Chemical Society, April 5, 1923.

¹⁰ Weiser, J. Phys. Chem., 22, 439, 480, 576 (1918).

For gaging the brightness of the luminescence of the compounds, several methods were used. In the earlier work, compounds were compared with the Moeller-Evans reaction. In later work, the fainter compounds were compared with a set of radio-luminous disks, which were carefully protected from light to prevent phosphorescence. These disks were calibrated by the Bureau of Standards; their brightness ranged from 1 to 8 microlamberts. The brighter compounds were compared by the optical pyrometer method described by Nichols. The ranges of the two methods overlap, so that it is possible to determine, at least approximately, the surface brightness of any luminescence. Another method of estimating brightness is given by Ives. The writers hope to say more concerning such measurements in a later article.

Factors not Determinative of Luminescence

It is very clear, as Lifschitz has pointed out, that reaction velocity is not the factor that determines the luminescence. The oxidations studied are all very slow compared to ordinary ionic reactions, which are not chemiluminescent at all. But if a given Grignard compound is luminescent, increased speed of reaction will brighten the light; for example, pure oxygen gives much more light than air with such Grignard compounds. The quantitative work of Amberson¹³ on luciferin, the luminescent material studied by Harvey, tends strongly to indicate that the brightness is closely proportional to the speed of oxidation. Results of the writers indicate further that the spectral band of a compound widens somewhat when the intensity is high. Thus the radiation from the Moeller-Evans reaction ordinarily photographs as if it were confined to the range 5200–3500, and was so reported by Evans and Dufford. But it is easy to show, when the intensity is high, that the band really extends to about 6200, on the red end, and probably beyond 3000 on the short-wave-length end.

The heat of oxidation of the compounds is also not determinative. Qualitative observations by the writers are in accord with the careful quantitative work of Lifschitz and Kalberer. In certain series of compounds the brightest become hottest during oxidation. But the reverse is more often true; the most of the remarkably bright compounds actually become cooler while oxidizing and radiating, because not enough heat is given off to compensate for the cooling due to the evaporation of ether.

It appears that slight changes in temperature do not affect the brightness of the luminescence appreciably.

Effect of Solvents

While much remains to be done in this line, enough evidence has been secured to establish clearly that the ethyl ether in which such compounds

¹¹ Nichols, Science, 55, 157 (1922).

¹² Ives, J. Franklin Inst., 194, 213 (1922).

¹³ Amberson, J. Gen. Physiol., 4, 517 (1922).

are usually made is by no means necessary. Much evidence indicates that these compounds exist as etherates in such solutions. Other ethers may be substituted, however, without destroying the luminescence; normal ethers appear slightly better than iso ethers, or than diphenyl ether, at least for bromine compounds. Chlorine Grignard compounds are usually best in iso-amyl ether. Dimethylaniline can be substituted for ether, though the light is less intense than with ethyl ether, as was shown by Lifschitz. Toluene containing some ether has been used also. Lifschitz states that the pure, ether-free Grignard compounds, even the aliphatic compounds, give light. The writers have not yet been able to verify this statement, but it is very clear that the nature of the solvent affects the intensity of the light. The writers have failed to find any effect on the spectral distribution, however, though several tests were made. The question should be investigated further before any final decision can be reached.

Effects of Other Oxidizers

The light is brightest when pure oxygen is used; air is much less effective. Other reagents, such as sodium peroxide, hydrogen peroxide, etc., react more violently, but they give no light. Water hydrolyzes these compounds instantly, but without evolution of light. Other gases, such as sulfur dioxide, carbon dioxide, nitric oxide, and nitrogen dioxide also give no light, although some of them react. Lifschitz and Kalberer reported evolution of light with benzene triozonide and also with nitrous oxide, but the writers failed repeatedly to observe light with this gas when particular care was first taken to remove all traces of atmospheric oxygen from the apparatus.

Effect of Other Metals

The magnesium of the Grignard compounds appears to be necessary for chemiluminescence. Several of the analogous zinc compounds, including phenylzine bromide and iodide, and p-bromophenylzine bromide. showed no light. Evans, in a private communication, has stated that he found no light with phenylmercuric bromide. The writers plan to try certain other compounds later.

Effect of Concentration

These compounds evolve most light when the concentration is fairly high; but when the concentration becomes too great, an optimum value is passed. For phenylmagnesium bromide the optimum lies near 2.5 moles per liter. For some other compounds the optimum is at higher concentrations. However, in at least one case, that of the Grignard compound from α -bromonaphthalene, the optimum is lower. This compound has a remarkable tendency to crystallize from solution. When its brightness has died down, successive additions of ether increase the brightness again.

Effect of Reacting Halogen

The identity of the reacting halogen definitely affects both the color and the intensity of the radiation. To test this point, solutions were prepared of the following Grignard compounds: C_6H_5MgI , $p\text{-}CH_3C_6H_4MgI$, C_6H_5MgBr , $p\text{-}CH_3C_6H_4MgBr$, C_6H_5MgCl , and $p\text{-}CH_3C_6H_4MgCl$. In these series the iodine compounds give the faintest light, while the chlorine compounds give the most. Further, the chlorine compounds give light that is distinctly greener than that from the other compounds, while the iodine compounds are bluest, that is, chlorides give off the longest effective wave length, and iodides the shortest. Fig. 1 shows the shift in wave

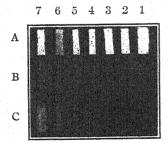


Fig. 1.—Luminescence of Monohalogen benzene Grignard compounds. A, white light; B, C₆H₅MgCl; C, C₆H₅MgBr. The numbers refer to the filters described in Table I

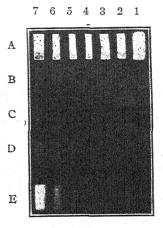


Fig. 2.—Luminescence of Grignard compounds from bromine derivatives of benzene with alkyl side-chains para to the reacting halogen. A, white light; B, C₆H₅MgBr; C, CH₃C₆H₄MgBr; D, C₂H₅C₆H₄MgBr; E, C₄H₉C₆-H₄MgBr

length for phenylmagnesium chloride and bromide; the light from the iodide was too faint to photograph in the same time of exposure. A somewhat similar effect is observed in the dihalogen derivatives, p-TC₆H₄MgI, p-BrC₆H₄MgBr, p-ClC₆H₄MgCl; the same shift in wave length is observed. The same brightness relations exist, except that the dichloro compound gives less light than the dibromo compound. The effect is due partly to the lower yields obtained from the dichloro compound; the point is being investigated further, to determine whether this is the only reason.

Method of Preparing Grignard Compounds Containing Chlorine

None of the chlorine compounds mentioned above can be prepared by the usual methods, in ordinary ether, at least not in any reasonable length of time. The di-iodo compound is also difficult to prepare. Evans⁸ has described a method for preparing the latter, using the analogous dibromo compound as a catalyst; but this method is open to the objection that the catalyst is itself luminescent and, hence, makes the tests unreliable. Hesse¹⁴ patented a method of making chlorine Grignard compounds using pinene hydrochloride as catalyst. The writers found that the compounds formed in *iso*-amyl ether with iodine or ethyl bromide as catalyst; this method works with the di-iodo compound also. The yields are probably somewhat less than with pinene hydrochloride, but the products give a brighter light, as if the pinene hydrochloride tended to inhibit the luminescence.

Effect of the Organic Radical

The character of the radiation during oxidation is profoundly affected by the nature of the organic radical involved. It may be true that ordinary saturated aliphatic compounds give light when crystallized, free from ether, but it is very certain that they do not do so in any ordinary solvent. It was thought at first that the luminescence was confined to aromatic compounds.

Certain theories regard the benzene ring as being in vibration. It appeared possible that the luminescence might be associated with some sort of vibration of the ring. If so, certain effects may be expected: first, that if the ring were loaded with a substituent group, the light should be affected regularly as the mass of the loading group increases, probably in the direction of an increase in wave length; and second, that symmetrical loading should not produce the same effect as unsymmetrical; probably the unsymmetrical (ortho and meta) compounds should show shorter wave lengths than the symmetrical (para) compounds, but without much difference in intensity. Other questions concerning the effect of structure and unsaturation also are suggested. The following paragraphs will show how these compounds actually behave.

Effect of Position of Substituted Group

In order to test carefully the effect of the position of the substituted group, a number of series of compounds were prepared which would form Grignard compounds differing only in the position of the substituted group. They included the *ortho*, *meta* and *para* derivatives of methylphenylmagnesium chloride, bromide and iodide, chlorophenylmagnesium chloride and bromo- and chlorophenylmagnesium bromide. The light

¹⁴ Hesse, Ber., 39, 1147 (1906); Chem. Zentr., 1906, I, 1424; 1908; Ger. Pats. 189,476 and 193,177.

from these compounds was studied carefully, both visually and photographically.

The results show that the para compounds are always very much brighter than the corresponding ortho or meta compounds, though neither of the latter classes is consistently brighter than the other. The differences in wave length are slight—rather less than might have been expected. Indeed, after examining the toluenes, the writers were in doubt whether the observed differences were real at all. The dichlorobenzene derivatives are so faint that their evidence is inconclusive. But the dibromobenzene and chlorobromobenzene derivatives show the same effect as the toluenes, and in so pronounced a form as to be unmistakable. While the differences are small, they are quite regular. Each compound radiates a spectrum made up of a wide continuous band. The spectra of the para compounds always extend farther toward the red than is the case with the other isomeric compounds; the ortho and meta compounds are more nearly alike, but the meta compounds regularly show the shortest wave lengths. Light from para compounds is, therefore, always greener than that from the others, and from meta compounds more violet. The differences show best in the dibromo and chlorobromo compounds; these are illustrated in Figs. 2 and 3, respectively.

Mass and Chemical Nature of Loading Group

Moeller⁵ concluded that the brightness of the luminescence is proportional to the molecular weight of the halogen derivatives. This statement is not true, even of the few compounds which he studied. To test this point, the writers studied a large number of compounds.

When the group added to the benzene ring is an aliphatic side-chain, then the brightness does increase with the weight of the added group or, what is the same thing, with the molecular weight of the compound. Thus, in the series C₆H₅MgBr, p-CH₅C₆H₄MgBr, p-C₂H₅C₆H₄MgBr and p-C₄H₉-C₆H₅MgBr, the brightness increases with the weight and, at the same time, the wave length shifts steadily toward the violet and not toward the red, as might be expected if mass were the determining factor (by analogy with the vibration of a loaded spiral spring). Fig. 4 shows the effect fairly well, except that the exposure for the toluene derivative was too short.

When the loading group is a halogen, however, the result is different. This was tested by studying series in which the loading halogen alone was varied, as in the following: $p\text{-}IC_6H_4MgBr$, $p\text{-}IC_6H_4MgI$, $p\text{-}BrC_6H_4MgBr$, $p\text{-}ClC_6H_4MgBr$, and $p\text{-}ClC_6H_4MgI$. In these compounds, the brightness of the radiation increases in most remarkable fashion as the weight of the loading halogen decreases, and with this, there is an increase in the effective wave length.

In the series p-C₂H₅C₆H₄MgBr, p-ClC₆H₄MgBr and p-(CH₃)₂NC₆H₄-MgBr, the masses of the loading groups are comparable, being 29, 35 and 44, respectively. The brightness shows no regularity; the chlorine derivative is by far the brightest, and the dimethyl-aniline derivative the faintest.

It has already been shown that in the case of Grignard compounds from monohalogen benzene derivatives, the brightness increases as the molecular weight decreases, and the wave length increases at the same time. Certain dihalogen derivatives were shown to behave likewise.

Among diphenyl derivatives, Schmidlin³ reports p-C₆H₆C₆H₄MgBr as giving a bright blue light; the writers find that p-p-BrC₆H₄C₆H₄MgBr gives a bright green light.

These results seem to indicate that mass is not at all the controlling factor in these compounds; if it has any effect, it is so small that it is

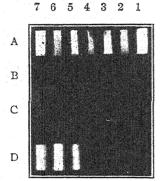


Fig. 3.—Luminescence of Grignard compounds from dihalogen derivatives of benzene. A, white light; B, o-BrC₆H₄MgBr; C, m-BrC₆H₄MgBr; D, p-BrC₆H₄-MgBr

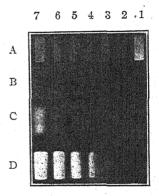


Fig. 4.—Luminescence of Grignard compounds from bromochlorobenzenes. A, white light; B, o-ClC₆H₄MgBr; C, m-ClC₆-H₄MgBr; D, p-ClC₆H₄MgBr

completely masked by other factors depending on the chemical nature of the loading groups. Further evidence on this point will be given later.

In this discussion it has been assumed that in dihalogen derivatives of benzene only one of the halogens reacts with magnesium to form a Grignard compound, and that when the 2 halogens are different, the magnesium reacts with bromine, if present, in preference to the other halogens, or with iodine in preference to chlorine. It is believed that these assumptions are in accord with the experience of most other workers in the field, as well as with many incidental observations by the writers.

Derivatives of Naphthalene, Anthracene and Xylenes

The Grignard compound from α -bromonaphthalene gives a blue light, nearly as bright as that formed in the Moeller-Evans reaction. That from

 β -bromonaphthalene is much brighter, and is at least as bright as that from the Moeller-Evans reaction. By analogy with the benzene derivatives, one might expect the Grignard compound from 1,4-dibromonaphthalene to be still brighter and bluer. In fact, it is much fainter, and greener. The Grignard compound formed from 1,4-chlorobromonaphthalene is, however, much brighter and bluer than that from the 1.4dibromonaphthalene compound. It, also, is about as bright as the light from the Moeller-Evans reaction. α-Chloronaphthalene forms a compound giving a light much weaker than the other compounds just mentioned, and too faint to photograph well.

Some of these effects are shown in Fig. 5.

9,10-Dibromo-anthracene forms a Grignard compound showing a greenish-blue light whose faintness A can hardly be due entirely to poor yields. Since this has a bearing on the probable structure of anthracene we intend to study the matter further.

If Moeller's conclusion as to the effect of mass were correct, the results obtained with the compounds just described would necessarily have been very different. Further, it is n evident that the behavior of these multiplering compounds, and perhaps also of the diphenyl compounds, is not altogether analogous to the behavior of the benzene deriv- E atives. Perhaps a more useful and fruitful point of view is to regard the a-bromonaphthalene Grignard compound as a bromo- nard compounds from naphthabenzene derivative with its ortho and meta positions both loaded; and the β -bromo compound as a similar derivative with the meta E, (1,4) CIC 10 HoMgBr and para positions substituted. According to

5 4 3 2 1

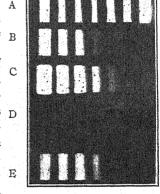


Fig. 5.-Luminescence of Griglene derivatives. A, white light; B, α-C₁₀H₇MgBr; C, β-C₁₀H₇-MgBr; D, (1,4)BrC10H6MgBr;

this view, the Grignard compound from 1,2-dimethyl-4-bromobenzene should be brightly luminescent. The writers were preparing to test this point, but came across the statement by Spath4 that the light from this compound is very bright. Other xylene compounds give less light; for example, those from 1,3-dimethyl-4-bromobenzene, and 1,4-dimethyl-2bromobenzene. It is hoped that other experiments in this direction will be ready for reporting soon.

Effect of Structure and Unsaturation

It will be noted that all the compounds so far mentioned as luminescent are cyclic in structure, and unsaturated. It is of interest to inquire whether the cyclic structure, or the unsaturation, or both, are necessary to produce luminescence.

Further evidence pointing toward unsaturation as being an important factor is the complete failure of saturated aliphatic Grignard compounds to show luminescence in ether solution. The following list of saturated nonluminescent compounds, containing both halogen-substituted and simple aliphatic derivatives, shows how widespread is the lack of luminescence: C₂H₅MgBr, C₂H₅MgI, C₃H₇MgBr, C₄H₃MgBr, *i*-C₅H₁₁MgBr, C₇H₁₅MgBr, ICH₂MgI, BrC₂H₄MgBr, IC₂H₄MgI. If molecular weight had anything to do with luminescence, some of the heavy molecules at the end of the list should give light, for they are comparable with the benzene ring in mass. This is one more reason for thinking that mass has nothing to do with the question, but suggests that unsaturation or cyclic structure may have some influence.

The cyclic structure alone, however, is not sufficient to give luminescence. Several saturated cyclic compounds which form Grignard compounds easily prove to be quite inactive, photochemically. Examples are: cyclo-C₆H₁₁Br, C₁₀H₁₅OBr (camphor), C₁₀H₁₇Cl (pinene hydrochloride).

Unsaturation alone is likewise not a sufficient condition for luminescence. Thus the following substances which are really phenyl-substituted aliphatic compounds give no light, though highly unsaturated: C₆H₅CH₂MgCl, C₆H₅CH₂MgBr, p-ClC₆H₄CH₂MgBr, (C₆H₅)₃CMgCl.

Careful scrutiny of the lists seems to indicate that the determining difference lies in the fact that in the luminescent compounds, the magnesium is attached directly to an unsaturated carbon atom, while in the others it is not. No exceptions to this statement are known at present.

To test this supposition further, the compound ClHC:CHMgCl was prepared, as an aliphatic compound with the supposedly necessary grouping. This compound is faintly but unmistakably luminescent. It is believed to be the first aliphatic compound discovered to be luminescent in ether solution. The analogous bromine compound, BrHC: CHMgBr. shows so much fainter luminescence that it is to be regarded as doubtful. but this is what would be expected if these compounds are like the monohalogen benzene Grignard compounds in their behavior. The Grignard compound from β-bromostyrene, (C₆H₅CH:CHBr), is fairly bright, however, thus substantiating the view. On the other hand, allyl bromide and iodide, which are unsaturated, but which have the halogen attached to a saturated carbon, give non-luminescent Grignard compounds. The final product of this reaction is claimed to be diallyl. As the reaction was in progress, oxygen was passed into the solutions in the dark, so that any allylmagnesium bromide or iodide present as an intermediate product would be oxidized. No light was observed. It is hoped to make other tests later.

Especially Bright Reactions

Several of the compounds are bright enough to be worthy of special mention. The Moeller-Evans reaction has been mentioned already; it is as bright as any of the classical chemiluminescent reactions, except the oxidation of luciferin. The Grignard compounds derived from α -bromonaphthalene, from 1,4-bromochloronaphthalene, and from ρ,ρ -BrC₆H₄C₆H₄Br, are nearly as bright. That derived from β -bromonaphthalene is at least as bright as the Moeller-Evans reaction, and probably brighter at its best. The compound ρ -ClC₆H₄MgBr is much brighter than any other so far found. Careful pyrometric measurements show that it is brighter even than luciferin, except possibly for the bright specks in the luciferin solution and, therefore, probably the brightest case of chemiluminescence on record. The comparisons were made at the wave length corresponding to the maximum of the emission of the luciferin. The light from the luciferin is greenish-blue, while that from the Grignard compound is deep blue. The ease of preparation of this compound and the high intensity of its light make it an ideal demonstration material for illustrating the phenomenon of chemiluminescence.

Reactions with Chloropicrin and Bromopicrin

Many of the luminescent Grignard compounds studied show light also when reacting with chloropicrin or with bromopicrin, as in the well-known Wedekind reaction. These cases are of interest as being probably not oxidations, though the precise nature of the reactions is not known. Thus far, the work of the writers has established several important facts regarding this type of luminescence. (1) No compound has been found to give light in these reactions that does not also give light on oxidation with oxygen. (2) The light obtained from chloropicrin is always stronger than that obtained with bromopicrin. (3) The light from these reactions is clearly not identical with that from the oxidation of the same Grignard compounds with oxygen. It is always of somewhat longer wave length, although its spectrum is always a single continuous band. (4) The order of brightness in these reactions is precisely the reverse of that for oxidation with oxygen; that is, with chloropicrin, iodides are the brightest, and chlorides the least bright.

An attempt was made to determine the part of the chloropicrin molecule that is essential for the production of light. Aliphatic nitro compounds, picryl chloride, chloroform and other compounds were tried, but none of these gave light, although some of them reacted violently with the Grignard reagent. Apparently there is something about the particular chloropicrin grouping that is necessary for the production of light in these reactions.

Fluorescence

A very large number of the oxidation products of these Grignard compounds show fluorescence in "near" ultraviolet light. Apparently little regularity is to be found in most cases. Several new multiple-banded

spectra have been observed. A few of these fluorescences are extremely bright; curiously, these all come from compounds that show very bright chemiluminescence with oxygen. In spectral distribution, the fluorescence is clearly not the same as the related chemiluminescence. These results the writers hope to discuss more fully in a later article.

List of Luminescent Grignard Compounds

Tables II and III give lists of the Grignard compounds studied by the writers, together with 2 or 3 others on which observations have been published by other workers. The list is believed to contain all known luminescent Grignard compounds except certain triple bond compounds investigated by Evans, on which the results have not yet been published. The notes indicate the cases where other investigators have studied any of these compounds, so far as is known. While most of the formulas as written are those generally accepted, they are written in this form here chiefly for reasons of brevity, and not because it is desired to claim that any particular structure has been proved. It may be that such results will come to be of aid in determining chemical structure later.

The spectral distributions, where given, are in terms of the windows listed in Table I. The picture so given is very incomplete, but any other method would require an unreasonable amount of space. Because of the difference in sensibility of the eye and the photographic plate, the apparent maxima as found by both methods are given.

The following substances showed no chemiluminescence with oxygen nor, in those that were tested, with chloropicrin or bromopicrin. Their oxidation products, however, frequently exhibited fluorescence; references to the latter are given for each formula. Where chemiluminescence was tested for only in the presence of oxygen the symbol O₂ is also added.

TABLE II
Non-Luminescent Grignard Compounds

	Fluorescence of oxidation			Fluorescence of oxidation
Compound	product	Ref.	Compound	product Ref.
(CaHa)2CMgCl	O ₂ Green	$3,7^{b}$	i-C5H11MgBr	5
ICH2MgI	O_2		iso-C5H11MgI	O_2 7^c
C2H4MgBr		5,7	C ₇ H ₁₅ MgBr	Bright blue
C2H4MgI	and the first of the second	3,7	C ₆ H ₆ ZnBr	O ₂
BrC2H4MgBr	O2 Green, blue		C ₆ H ₆ ZnI	O ₂
C ₈ H ₇ MgCl	O_2	7°	p-BrC6H4ZnBr	$O_2{}^a$
C3H7MgBr	O2	5,7	C6H6CH2MgCl	O_2 3
C ₂ H ₇ MgI	O2	7.°	C6H6CH2MgBr	5,7
iso-CaH7MgI	O ₂	7°	p-ClC6H4CH2MgBr	Blue
H2C = CHCH2Mg	Br Blue, green		cyclo-C ₆ H ₁₁ MgBr	7
H2C:CHCH2MgI	Faint green		C10H15OMgBr (Camphor)	$O_2{}^a$
C4H9MgBr	O ₂		C10H16HMgCl (Pinene hydr.)	Blue
IsM.H. ToMeT	0.	70		

[&]quot; Tested with chloropicrin also.

In Table III are listed the substances that showed chemiluminescence.

b In iso-amyl ether.

e Not prepared by the writers.

TABLE III

LIST OF LUMINESCENT GRIGNARD COMPOUNDS

		CCIACO ME		Comment of the Commen		of participation
Compound	ess	Spectral	Maximum is, photogr.		with bromopicrin	product
HC:CHMgCl			•		None	Pale blue
HC:CHMgBr H5CH:CHMgBr	Very faint Fair, blue		•	7	W Cint	Light blue
H ₆ MgCl	Bright green Bright blue		Œ	Faint Faint ¹	Very faint	Green
H _b MgI	Fair, blue	4-0	:	Windows 3-5	raint	Blue
CIC,H,M;CI	Paint green-blue		: :			Blue, green Blue, green
BrC6H4MgBr	Fair, bluish	2 G3 (13.	***		Yellow-green
BrC6H4MgBr	Yery bright blue	, -	6	Very faint	None	Green, blue
IC,H,MgI ClC,H,MgBr	Faint Bright blue	-,-,-	5,6 7	None		Deep green
-CIC ₀ H ₄ MgBr	Bright blue Exceedingly bright blue	32 GO	67	Faint	None	Yellow-green Very bright blue
CIC ₆ H ₄ MgI	Bright blue	3-7	10:		NT.	Bright green
IC5H4MgBr CH3C4H4MgCl	Fair, greenish	3-77		Fainc	Mone	Green
CH ₃ C ₆ H ₄ M ₂ C ₁	Faint, greenish	3-7		None		Green Blue, vellowish
CH3C6H4MgBr	Faint, green-blue	00 g	F6 7:	Faint	Faint	Green
-CH3C6H4MgBr CH3C6H4MgBr	Fair, green-blue Bright, green-blue	37	1-6 7	Faint		Green
CH ₃ C ₅ H ₁ MgI	Fair, bluish	33 33 7 7	೨೦ ೮೮	Fair, bluish Bright vellow-green	None Faint	Yellow-green
CH ₃ C ₆ H ₄ MgI C ₅ H ₄ C ₆ H ₄ MgBr	Bright, bluish Bright blue	3-7	i-6 7	Bright green Faint	None Faint	Bright blue-green Bright blue-green
$(CH_3)_2NC_6H_4MgBr$	Bright blue Faint blue	3-6		None	None	Deep bine, bright
$C_0H_5C_0H_4M_{f g}B_{f r}$ $D_0B_{f r}C_0H_4C_0H_4M_{f g}B_{f r}$	Bright blue Bright green	3-7	:			Green, blue
,2) (CH ₃) ₂ C ₆ H ₃ (4) Mg Br ,3) (CH ₃) ₂ C ₆ H ₃ (4) Mg Br	Bright yellow-white Faint, blue	3-7	:			Bright blue
$(CH_3)_2C_6H_3(2)MgBr$ $C_{10}H_7MgCl$	Faint, blue Fair, green-blue		:			Blue
C10H7MgBr	Bright greenish-blue Very bright, blue		515 66 77	None	None	Blue-green Very bright blue
4) BrC10HeMgBr 4) CIC10HeMgBr	Fair, green-blue Bright green-blue		5, 6 5, 6	None	None	Blue-green Blue-green Green
a In iso-amyl ether. b Investigated independent	ntly by W. V. Evans.					
· d Too faint to allow accu	trate measurement of the v	wave len	gths.			
	Compound CHC:CHMgC! HHC:CHMgBr CHLCH:CHMgBr CHLCH:CHMgBr CHLAMgBr CHLAMgBr CHLAMgBr CHLAMgBr -CHCHAMgBr -CHCHAMgBr -HCHAMgBr -HCHACHAMgBr -HCHAMGBr -HCHAMgBr -HCHAMgBr -HCHAMgBr -HCHAMgBr -HCHAMgBr -HCHAMgBr -HCHAMgBr -HCHAMgBr -HAMgBr -H	Brightness Bry Faint Faint blue Faint greenish Col Faint, greenish Col Faint, greenish Faint, green-blue Faint, green-blue Faint, blue Faint, bl	Brightness Spectral color range Sight Grant Gran	Bright these range vis. phetral Maxin color range vis. phen is green blue Fair, blue Fair, blue Fair, blue Fair, blue Fair, blue Fair, blush Fair, greenish Fair, greenish Fair, greenish Fair, green-blue Fair, green-blue Fair, green-blue Fair, green-blue Fair, green-blue Fair, blush Fair, blue Fair, green-blue Fair, green-blue Fair, green-blue Fair, green-blue Fair, blush Fair, blush Fair, blush Fair, blush Fair, blue S-7 5, 6 7 5, 6 7 5, 6 7 5, 6 7 7 5, 6 7 7 5, 6 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	Bright these spectral Maximum range vis photogri color range vis photog	Brightness spectral Maximum brightness braint stage vis. Photogr. Chloropictin braint chloropictin braint with the Bright blue and a second stage vis. Photogr. Chloropictin braint green blue and a second stage vis. Photogr. Chloropictin braint green and a second stage vis. Photogr. Chloropictin braint green and a second stage vis. Photogr. Mone and a second stage vis. Photogr. None a second stage vis. Photogr. Second stage vis. Photography vis. Photograp

Summary

- 1. Grignard reagents in ether solution are chemiluminescent on oxidation by oxygen only if the magnesium is attached directly to an unsaturated carbon atom. This rule is shown to hold for both aliphatic and aromatic compounds, in all cases investigated.
- 2. The nature of the solvent affects the intensity of the luminescence, but apparently not the wave length.
- 3. No chemiluminescence is found when zinc or mercury is used instead of magnesium.
- 4. The wave length and intensity of the radiation are affected by the nature of the reacting halogen.
- 5. The wave length and the intensity are affected by the nature of the organic radical involved, and especially by the nature of substituted groups in the cyclic compounds. The effect depends on (a) the position of the substituent group; (b) the chemical nature of the substituent group. It is shown that the mass of the substituent is not the controlling factor.
- 6. Certain cases of very bright chemiluminescence are described; the luminescence of p-chlorophenylmagnesium bromide is believed to be the brightest yet recorded.
- 7. A method (apparently new) of preparing chlorine-containing Grignard compounds is described.
- 8. Many Grignard compounds give light when treated with chloropicrin and with bromopicrin. This light is not the same as that given out on oxidation with oxygen.
- 9. Many Grignard compounds and especially their oxidation-products are found to be fluorescent in ultraviolet light.
- 10. Two tables are given listing the luminescent properties of more than 60 compounds, of which over 40 are luminescent.

COLUMBIA, MISSOURI

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION AND DETERMINATION OF POTASSIUM AND SODIUM. A PERCHLORATE PRECIPITATION PROCESS USING NORMAL BUTYL ALCOHOL.

By G. Frederick Smith Received June 14, 1923

The perchlorate method for the separation and determination of potassium and sodium has been quite generally accepted as a satisfactory substitute for the chloroplatinate procedure. The use of absolute ethyl alcohol in the perchlorate procedure is a pronounced disadvantage. The method has the further disadvantage of being an extraction process. This method of extracting a mixture of salts with a solvent for one of them is necessarily inefficient, since the crystals of one may be more or less sur-

rounded by a coating of the other salt. It would obviously be a considerable improvement if the use of ethyl alcohol and the inefficient extraction type of procedure could be entirely eliminated. The present paper shows how both of these improvements can be accomplished and also simplifies the procedure with consequent increase in accuracy.

Studies in the improvement of the perchlorate separation of potassium and sodium are desirable, as indicated by recent work in the field by several careful observers including those of Baxter and Kobayashi, Baxter and Rupert² and Gooch and Blake. The most complete work on the perchlorate method is that of Morris⁴ which contains an extensive bibliography. Few further references to the literature of the subject are therefore necessary here.

The Method

The process, in brief, consists in the precipitation of potassium perchlorate from solution in warm water, in the presence of sodium perchlorate, by the slow addition of a proportionally large volume of N-butyl alcohol containing $0.5{\text -}1\%$ of perchloric acid dihydrate. The solution together with the precipitated potassium perchlorate is then boiled for 30 seconds, cooled to room temperature and filtered using a Monroe or Gooch crucible. The precipitate is washed with butyl alcohol, dried at $150{\text -}250^{\circ}$ for 1/2 to 1 hour and weighed as potassium perchlorate. The sodium is determined in the filtrate by evaporation of the solvent and conversion of the sodium perchlorate to sulfate, and is weighed as such in the usual manner. The method is best suited to the determination of sodium by difference, after weighing the mixed potassium and sodium chlorides.

Preparation of Materials

Normal Butyl Alcohol.—This material is readily obtainable on the market at the present time at a moderate price. The alcohol used in this research had a boiling range of $112-118^{\circ}$; d_4^{25} 0.8065. It was distilled as received without further treatment, and the first and last 5% discarded.

Perchloric Acid.—The acid used was prepared by the method of Willard.⁵ This material was converted to the true dihydrate,⁶ HClO₄-2H₂O by a method to be described in a subsequent paper. The dihydrate was used to acidify the butyl alcohol employed in this investigation as well as for converting weighed portions of potassium and sodium chlorides to perchlorates.

Sodium and Potassium Perchlorates.—These materials were prepared

- ¹ Baxter and Kobayashi, This Journal, 39, 249 (1917); 42, 735 (1920).
- ² Baxter and Rupert, ibid., 42, 2048 (1920).
- ³ Gooch and Blake, Am. J. Sci., 44, 381 (1917).
- ⁴ Morris, Analyst, 45, 349 (1920).
- ⁵ Willard, This Journal, 34, 1480 (1912).
- 6 70% perchloric acid may be used wherever this material is mentioned in this paper.

from sodium and potassium chlorides that had been twice recrystallized from aqueous solution using hydrogen chloride. The chlorides thus obtained were converted to perchlorates with an excess of pure perchloric acid followed by crystallization of the perchlorates and filtration with centrifugal drainage. The perchlorates thus obtained were dried at 250° and were found to be free from chlorides.

Sodium and Potassium Chlorides.—These were a foreign firm's best product dried at 250° before use.

Solubility Determinations

The solubilities of sodium perchlorate in n-butyl alcohol both at ordinary temperature and at the boiling point of the resulting solutions, in the absence and in the presence of increasing percentages of perchloric acid, are important in connection with the present investigation. Solubility tubes were prepared containing an excess of anhydrous sodium perchlorate together with the pure butyl alcohol or alcohol containing 0.25%, 0.5% or 1.5% of perchloric acid dihydrate by weight. The sealed glass tubes were revolved endwise during 5-6 hours at room temperature of 25° with variation of less than 3°. The temperature coefficient for the solubilities involved was known to be high, but since all experiments were conducted simultaneously and comparative results only were desired, accurate temperature control was not necessary. The saturated solutions thus obtained were allowed to settle, samples were withdrawn from the clear supernatant liquid and the sodium perchlorate was determined as described by Willard and Smith.7 The solubility determinations of the same solutions at the boiling point were carried out in a specially prepared all-glass refluxing apparatus. The solutions in presence of excess of solute were gently boiled for 1/2 to 1 hour and samples were withdrawn from the continuously boiling solution with a special pipet provided with a filtering medium in its lower stem and maintained hot by being inserted through the reflux condenser into the hot vapors over the solution.

The results obtained are reported by graph (Fig. 1) rather than by table to avoid a wrong conclusion concerning their accuracy. The determinations were carried out in duplicate to exclude the possibility of gross error.

By study of the values reported in Fig. 1 it is seen that the solubility of anhydrous sodium perchlorate at 25° in the butyl alcohol employed is approximately 3%. The addition of 0.25%, 0.5% and 1% perchloric acid dihydrate is progressively without appreciable effect, the solubility still remaining approximately 3% in the presence of 1% of acid. The solubility of sodium perchlorate in the pure alcohol at the boiling point of the solution is approximately 7.6% while with addition of perchloric acid dihydrate the solubility increases uniformly until at 1% acid concentration the solu-

⁷ Willard and Smith, This Journal, 45, 291 (1923).

bility of the sodium salt has reached approximately 9%. In addition to the values included in Table I it was found that the butyl alcohol when treated with 1% of water by volume and 1% of perchloric acid dihydrate by weight, dissolved at 25° approximately 4.5% of sodium perchlorate, and this value was increased to approximately 5% for butyl alcohol containing 1% of acid and 3% of water for the same temperature. It has been shown by Willard and Smith⁷ and by Gomberg⁸ that equilibrium for solutions of perchlorates in organic solvents is slowly attained and that there is a pronounced tendency towards supersaturation. This observation was found to hold for the solution of sodium perchlorate in butyl alcohol, so that in actual practice solubilities in excess of those given are

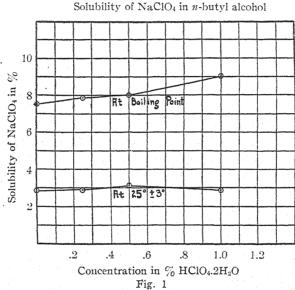


Fig. 1 often obtained. Determinations of solubilities of sodium perchlorate in butyl alcohol containing 1% of perchloric acid dihydrate with 1% and 3% of water at the boiling point were not made but the values are known to be much higher than for the same solutions without water and at the

The solubilities of potassium perchlorate in the same solvent were made omitting determinations for boiling solutions. In these determinations 100 cc. or more of solvent was employed, the solutions resulting from the equilibria attained after 5–20 hours' agitation were filtered through a Monroe crucible and the potassium perchlorate in the weighed filtrates was recovered and converted to potassium sulfate, from the weight of which the potassium perchlorate originally dissolved was de-

boiling temperature.

⁸ Gomberg, This Journal, 45, 403 (1923).

termined. The determinations were carried out in duplicate and the results of these closely agreeing duplicates are reported in Table I.

TABLE I

The Solubility of Potassium Perchlorate in n-Butyl Alcohol with and without Various Additions of Water and Perchloric Acid

Perchloric acid added as $HClO_4.2H_9O$ in parts by weight. Water was added in parts by volume. Temperature, $25^\circ \pm 3^\circ$.

Additions to bu Acid % +	ityl alcohol Water %	Amount of solution analyzed Cc.	K ₂ SO ₄ found G.	KClO₄ dissolved ^a Mg./100 cc.
None	None	125	0.0010	1.35
0.25		110	.0007	1.0
0.5		102	.0007	1.0
1.0		115	.0006	1.9
	1.0	96	.0012	2.0
1.0	1.0	98	.0008	1.4
• •	3.0	100	.0023	3.8
1.0	3.0	95	.0010	1.6
0.5	3.0	84	.0006	1.2
1.0	5.0	97	.0014	2.3

One-third of these values represents the amount calculated as K₂O.

It will be seen from Table I that for butyl alcohol, as demonstrated for ethyl alcohol by Thin and Cumming⁹ and by Baxter and Kobayashi,¹ the solubility of potassium perchlorate is materially diminished by the addition of perchloric acid. This effect is very pronounced for butyl alcohol containing up to 5% of water. The data of Table I led to the choice of butyl alcohol containing 1% of perchloric acid dihydrate and 3% of water as the best solvent to be used in the separation and determination of potassium and sodium in the manner to be described.

The Precipitation of Potassium Perchlorate and Separation from Sodium Perchlorate

The mixed chlorides of potassium and sodium (free from sulfate) obtained by the J. Lawrence Smith or other method are evaporated to dryness with an excess of perchloric acid. A second evaporation is desirable when the amount is great. Two or three cc. of water is then added according to whether the amount of potassium is low or high, respectively, and the mixed perchlorates are then dissolved by gently swirling the covered beaker over a free flame. The sodium perchlorate is extremely soluble. Potassium perchlorate dissolves to the extent of 20 mg. per cc. at 25° as shown by Willard and Smith⁷ and more than 200 mg. at 99° as shown by Calzolari. Sixty-five or 100 cc. of 0.5–1.0% perchloric acid butyl alcohol solution, according to whether 2 cc. or 3 cc. of water has been added to dissolve the mixed perchlorates, is heated to boiling (using a wire gauze

⁹ Thin and Cumming, J. Chem. Soc., 107, 361 (1915).

¹⁰ Calzolari, Acc. Sci. Med. Ferrara, 85, 150 (1911).

and free flame) and added to the warm, aqueous, perchlorate solution slowly with vigorous stirring. The potassium perchlorate is slowly precipitated as the addition of alcohol continues and after all has been added the solution is boiled gently in the covered beaker for half a minute and cooled to room temperature.

The resulting solution and precipitate are filtered through a weighed Monroe or Gooch crucible, the potassium perchlorate is transferred and the beaker walls are rinsed with the butyl alcohol solution used as precipitant (for precautions involved in the preparation of Gooch crucible asbestos for acid butyl alcohol solutions and other manipulative details, see Willard and Smith).¹¹ The precipitate in the crucible is washed with 8 to 10 portions of 1 to 2 cc. each of precipitant, thus limiting the filtrate and washings to 125–150 cc. It is dried at 150–250°, cooled and weighed. From the weight of the perchlorate obtained, the potassium chloride or oxide present is calculated.

The filtrate and washings from the determination of potassium are diluted with considerable water, forming 2 layers, and the whole is evaporated on the steam bath in such a way as to avoid any condensation on the upper part of the beaker, thus hastening the evaporation. It is well to add 5 to 10 cc. of water at the end of the evaporation to make the removal of organic matter more complete as the solution becomes concentrated. By such treatment a colorless residue of sodium perchlorate and perchloric acid can be obtained. When any brown color remains after this treatment. remove the watch glass supports and heat the beaker gradually on the hot plate until fumes of perchloric acid are evolved. Allow the perchloric acid to continue just at the fuming point until the organic matter is oxidized. Add a few drops of perchloric acid if not enough is present. When the brown color is removed 0.5 cc. of concd. sulfuric acid is added, the watch glass supports are replaced and the acid is fumed off using a wire gauze and free flame. The beaker is cooled, 5-10 cc. of water added and the cover glass and beaker walls are washed. The sodium sulfate solution is then transferred to a platinum crucible, previously weighed with cover, the solution evaporated and the sodium sulfate ignited as usual.

The separation of potassium and sodium perchlorates by the process given was tested by the analysis of 10 mixtures of potassium chloride and sodium chloride and the results are reported in Table II.

Table II shows that small or large amounts of potassium can be separated from large or small amounts, respectively, of sodium by one precipitation, results being obtained which agree excellently with the calculated values. An exceptional compensation of errors accounts for this fact. The amount of potassium perchlorate dissolved which would make results low is counterbalanced by the occlusion of sodium perchlorate.

¹¹ Willard and Smith, This Journal, 44, 2823 (1922).

In all cases except those in which a very small amount of sodium is present no solubility correction for potassium is necessary. Direct determination of sodium in the filtrate from potassium gives results somewhat high in accordance with the higher molecular weight of potassium sulfate than that of sodium sulfate. The average plus and minus errors for the 10 analyses of Table II show the potassium chloride found to be 0.2 mg. low

Table II

The Separation and Determination of Potassium and Sodium

KCl taken G.	KCI found G.	Error KCI G.	NaCl taken G.	NaCl found G.	Error NaCl G.
0.0083	0.0085	+0.0002	0.4256	0.4251	-0.0005
.0136	.0134	0002	.2545	-2550	+ .0005
.2024	.2017	0007	.2066	.2075	+ .0009
.0536	.0537	+ .0001	. 1995	.1999	+ .0004
.1063	.1066	+ .0003	$.1558^{a}$.1567	+ .0009
.1012	.1006	0006	.1500	.1503	+ .0003
.1511	.1513	+ .0002	.1001	.1007	+ .0006
.2019	.2017	0002	$.0550^{a}$.0564	+ .0014
.2019	.2015	0004	. 0505	.0512	+ .0007
.4010	.4001	0009	.0049	.0058	+ .0009

^a These determinations are high because of an obvious contamination of the sodium sulfate during its recovery.

for an average sample of 0.1441 g. of KCl and the sodium chloride found 0.6 mg. high for an average sample of 0.1603 g. of NaCl.

The use of 2 to 3 cc. of water to dissolve the mixed perchlorates of potassium and sodium followed by precipitation of the former by addition of butyl alcohol, requires more alcohol than the familiar extraction process. It was thought that the use of an excess of water over that required to dissolve sodium perchlorate and partially dissolve potassium perchlorate when present in large amount, would require the use of less alcohol without much decrease in accuracy as compared with the determinations listed in Table II. The determinations reported in Table III were made with 0.75

TABLE III

THE SEPARATION AND DETERMINATION OF POTASSIUM AND SODIUM BY A MODIFIED PROCEDURE USING LESS BUTYL ALCOHOL

KCl taken G.	KCI found G.	Error KCl G.	Filtrate and washings Cc.	NaCl taken G.	NaCl found G.	Error NaCl G.
0.4005	0.4000	-0.0004	53	0.0061	0.0067	+0.0006
.2010	.2009	0001	57	.0501	.0502	+.0001
.1515	. 1514	0001	55	.1000	.1004	+ .0004
.1028	. 1026	0002	50	.1492	.1490	0002
.0506	.0509	+ .0003	47	.2001		
.0058	.0062	+ .0004	48	.2524	.2518	0006
.0094	.0099	+ .0005	53	.3998		
.2004	.2006	+ .0002	57	.2019	.2017	0002

cc. of water and 25 cc. of butyl alcohol containing 0.5% of perchloric acid dihydrate to precipitate the potassium perchlorate, all other conditions being the same as previously described.

As will be seen from Table III results obtained using less alcohol, while not as good as those included in Table II, are still satisfactory.

Because of the low vapor pressure of butyl alcohol at water-bath temperatures, which must not be exceeded, direct determination of sodium as sulfate is comparatively slow and rather inconvenient. Since the determination of potassium is far more important than that of sodium, which is usually determined by difference following the determination of the mixed chlorides of potassium and sodium, and since by the method given the determination of potassium leaves nothing to be desired as to accuracy, the process is thought to be entirely adequate.

The correction for the solubility of potassium perchlorate to be applied in the absence of sodium was determined by precipitating 3 cc. of a saturated aqueous solution of potassium perchlorate in the manner already described, followed by filtration of the precipitated perchlorate and determination of the potassium in the filtrate. By duplicate analyses this correction was found to be 1.1 mg. of potassium perchlorate or 0.38 mg. of potassium oxide per 100 cc. of solution. This value is somewhat lower than that given in Table I but corresponds more exactly to working conditions.

The method as described has the following advantages: (1) absolute ethyl alcohol is replaced by n-butyl alcohol; (2) purification or dehydration of the alcohol used is not necessary; (3) it is a precipitation process; (4) one precipitation only is required; (5) the errors involved compensate one another exceptionally well.

A method has been devised by Willard and Smith¹¹ for the separation and determination of sodium and lithium using n-butyl alcohol. In this method butyl alcohol, used as received, was found adequate. The sodium was precipitated as chloride from its solution as perchlorate in butyl alcohol. The data described in the present paper indicate that butyl alcohol might be employed advantageously in an extraction process for the separation of potassium from sodium. Butyl alcohol could then be employed in the separation, successively, of potassium, sodium and lithium. The process is now being studied in this Laboratory.

The analyses reported in this paper include all of those carried out in the study of this method, with no omissions. The reliability of the process is thus demonstrated. No violent reactions were encountered throughout this work.

Summary

1. A method has been developed for the separation and determination of potassium and sodium depending upon the precipitation of potassium perchlorate from an aqueous solution by the addition of a comparatively

large volume of n-butyl alcohol, and its accuracy has been shown by its application to known mixtures of potassium and sodium chlorides.

- 2. The solubilities of potassium and sodium perchlorates in *n*-butyl alcohol have been determined.
- 3. The method was successfully applied in the separation and determination of known mixtures of potassium and sodium chloride including 20 determinations duplicating practical working conditions.
- 4. The method is particularly well adapted to the determination of potassium in the combined chlorides, the sodium being obtained by difference.
- 5. The use of n-butyl alcohol in proposed work on the separation and determination of potassium, sodium and lithium is discussed.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE HEATS OF VAPORIZATION OF MERCURY AND CADMIUM

By Mayor F. Fogler¹ with Worth H. Rodebush Received June 16, 1923

Probably the application of the quantum theory that is of most importance to physical chemists is the calculation of the entropies of the monatomic gases. The expression 1.5 relating the vapor pressure of a monatomic liquid to its heat of vaporization also promises to be an application of considerable significance. While it is probable that the numerical results furnished by the quantum theory in these cases will be more exactly confirmed by more accurate data as in the case of other triumphs of the quantum theory, nevertheless there is always a danger in generalizing from meager or uncertain data.

The two elements that offer the best opportunity for a check upon the equation for the entropy of a monatomic gas are mercury and cadmium. The specific heats of these metals have been determined with considerable accuracy both for the solid and liquid, and the heats of fusion are known. There is, however, no direct determination of heat of vaporization of any metal described in the literature, that appears to be at all reliable. It is possible to calculate heat of vaporization from vapor-pressure data by means of the thermodynamic relation,

$$\frac{\mathrm{d}\ln p}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{1}$$

¹ This communication is an abstract of a thesis submitted by M. F. Fogler in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Tolman, This Journal, 42, 1185 (1920).

³ Lewis, Gibson and Latimer, *ibid.*, 44, 1008 (1922).

⁴ Dushman, ibid., 43, 397 (1921).

⁵ Rodebush, ibid., 45, 606 (1923).

However, the above equation can be used with exactness only at low pressures, which is precisely where the data are subject to the greatest percentage errors. Since it involves the slope of a curve it requires, for an accurate determination, an empirical equation representing the data to be set up and differentiated. In the case of mercury, Smith and Menzies⁶ and Menzies⁷ have set up an empirical equation for which they claim an accuracy of 1% at temperatures above 120°. In their equation. there is no term to take care of the variation of the specific heat of liquid mercury with the temperature and, assuming that the accuracy is no greater than they claim, the heat of vaporization calculated at 298° K., from their equation might easily be in error by some hundreds of calories. 300 calories is one entropy unit at 25° C. and is a great enough amount to invalidate any generalization in regard to the entropy of monatomic gases. Since the heat of vaporization is not only the most uncertain factor in the calculation of the entropy of monatomic gases from the experimental data, but is also the fundamental quantity in the equation of Rodebush⁵ for the vapor pressure of monatomic liquids, it seemed desirable to make as accurate a determination of it as possible for mercury and cadmium.

Experimental Part

Some time was spent upon what promised to be a simple and rapid method of determining heats of vaporization at higher temperatures. This method consisted in dropping an iron plummet of known specific heat and known initial temperature into the vapor of the boiling metal and determining the weight of metal which condensed upon the plummet. It did not appear feasible to weigh the plummet while suspended in the vapor, although this could probably have been done, so that, after sufficient time had elapsed for the plummet to come to the temperature of the vapor, the vapor was swept away by a current of gas and the plummet was withdrawn and weighed. This operation was not difficult to carry out but the amount of metal collected depended on the time that the plummet was left in the vapor, indicating that the plummet was losing heat by radiation. Radiation shields were introduced in an attempt to remedy this difficulty, but the results were still very uncertain and variable. Apparently, at higher temperatures the transfer of heat by radiation is so rapid that the unavoidable slight difference in temperature between plummet and environment caused serious heat losses.

It was then decided to attempt to use for mercury a modification of the method employed so successfully by A. W. Smith⁸ to determine the heat of vaporization of water. In principle, this method consists in determining the difference in the rate of input of electrical energy required

⁶ Smith and Menzies, This Journal, 32, 1434 (1910).

⁷ Menzies, ibid., 41, 1783 (1919).

⁸ Smith, Phys. Rev., 34, 173 (1911).

to maintain a quantity of liquid in an insulated vessel at a constant temperature when vaporizing at a measured rate and when no distillation occurs. Smith maintained the water at a temperature just below its boiling point and controlled the distillation by bubbling a current of air through the liquid. It seemed undesirable to work with mercury near its boiling point because of the difficulty of preventing excessive heat losses due especially to radiation at high temperatures. It seemed better to work at the lowest temperature at which the mercury could be readily vaporized and this temperature was found to be about 140° where the vapor pressure of mercury is slightly greater than 1 mm. At this low pressure, the distillation could not be controlled by bubbling a current of inert gas through the mercury because it would be necessary to pass through so many moles of gas to each mole of mercury vaporized that serious errors would be introduced because of the heat capacity of the gas itself. Accordingly, the vaporization was controlled by distilling the mercury in a closed system maintained at constant pressure. When it was desired to commence the distillation the pressure was lowered until the mercury just began to vaporize; distillation was stopped by admitting gas and raising the pressure. The operation then consisted in bringing the vessel containing the mercury to a constant temperature, measuring the rate of input of electrical energy necessary to maintain this temperature for an indefinite time, then commencing the distillation and again measuring the rate of input of electrical energy necessary to maintain the same temperature as before, and the amount of mercury distilled in a given time.

The vessel containing the mercury to be distilled was placed in a Dewar tube, but in order to make the heat losses as small as possible, it was found desirable to place this part of the apparatus in some sort of a thermostat. An air thermostat was tried using a heating coil, fan stirrer, and an air thermometer regulator. It was not found possible to maintain uniform temperatures throughout this thermostat. Presumably an air thermostat can be kept at a uniform temperature provided the insulation of the walls is sufficiently good, but with our apparatus it was necessary to have so many openings through the walls that the insulation was poor and the regulation of the thermostat very unsatisfactory. A very satisfactory substitute was found in a vapor bath of dibutyl ether, which boils at 142°.

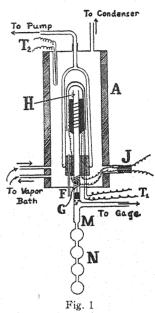
In Fig. 1 the general set-up of the apparatus is shown.

The vapor bath was made of copper with insulation (A) on the outside. H is the tube containing the mercury to be vaporized. The heating coil was wound around this tube, sheet asbestos was placed over the heating coil as insulation, and a sheath of heavy sheet copper was placed over the asbestos in order to equalize the temperature in different parts of the tube. A thermocouple was attached to the middle of this sheath. The tube H was about 10 cm. long by 2.5 cm. inside diameter; the vapor outlet was a tube of about 7 mm. diameter which was sealed through the bottom of the tube containing the mercury with a ring seal. The level of the mercury in the bulb was kept about 1 cm. below the

opening of the vapor tube, and experiments made with the apparatus exposed to view showed that the boiling was not violent enough to throw any drops of liquid mercury into the vapor outlet. The tube H was placed in the Dewar tube which was inverted because it was necessary to maintain the temperature inside slightly higher than the temperature of the vapor bath in order that no vapor might condense inside it. The mouth of the Dewar tube was closed with a loosely fitting cork. In order to make sure that no dibutyl ether vapor might enter the Dewar tube and condense, a very slow current of air was kept passing in through the tube F. To maintain the very highest possible vacuum at all times in the Dewar tube it was connected through a liquid-air trap to a mercury-vapor pump, which in turn was connected to a large evacuated flask, thus eliminating the sup-

porting pump. T_1 and T_2 are thermocouples. G is a magnetic plunger to dislodge any mercury that might condense on the sides of the tube, and N is a series of bulbs in which the distilled mercury was collected, sealed, and weighed. The connections to the heating coil were brought in at J. The source of the heating current was a lead storage battery. The energy input was measured by an ammeter and voltmeter calibrated to 0.1%. Pyrex glass was used exclusively in the apparatus. The mercury was carefully purified.

The arrangement of a Dewar tube inside of a vapor bath as described above gives a maximum of insulation with a minimum heat capacity. This is a very important consideration in an apparatus where it is necessary to maintain steady thermal conditions. It would be possible to decrease the heat losses by the use of insulating material, but such an apparatus would be unwieldy because of the length of time necessary to establish a steady state, and it is more important that the heat loss be constant than that it be small.



The mode of operation was as follows. The apparatus was brought to the temperature of the vapor bath, and the pressure in the tube containing the mercury was lowered until the mercury just began to distil. The heating current was adjusted to maintain a temperature inside the Dewar tube slightly above the temperature on the outside. When steady conditions had been established, any mercury adhering to the sides of the vapor outlet tube was dislodged by the magnetic plunger, collected in the bottom bulb, sealed off, and discarded. At the same time a stop watch was started, and at intervals of 15 minutes the mercury was collected in successive bulbs, sealed off and weighed. In the meantime, the current and voltage were maintained constant. No error was involved in the measurement of the time at which the bulb was sealed off, because after the mercury had been shaken down into the bottom bulb with the magnetic plunger, the next portions of mercury which came over would condense in the upper

part of the tube. As many as 5 bulbs were filled in succession. At the close of a run the pressure was raised to stop the distillation of the mercury and the current was readjusted to maintain the same temperature inside the Dewar tube as before, in order to correct for heat losses. Runs were made with temperatures inside the Dewar tube ranging all the way from 0° to 7° above the outside temperature. The correction for heat loss appeared to vary consistently with the temperature difference, being zero when the temperature difference was zero, and small in all cases. The value obtained for heat of vaporization appears to be quite independent of the correction made for heat loss. The results of 25 con-

Table I
Heat of Vaporization of Mercury

	****			COLL	
Temp. of vapor bath °C.	Temp. inside of Dewar app. °C.	Heat input Cal.	Heat loss Cal.	Wt. of Hg G.	ΔH for Hg Cal.
140.2	142.4	398.48	41.25	5.0670	14,140
140.2	142.4	398.48	41.25	4.9105	14,590
140.2	143.4	398.48	41.25	4.9100	14,595
142.0	145.0	342.3	54.1	3.9690	14,565
142.0	145.0	362.2	54.1	4.2185	14,650
142.0	144.0	363.9	39.0	4.4545	14,610
142.0	144.0	9.868	. 39.0	4.4930	14,505
142.0	144.0	363.9	39.0	4.5060	14,465
140.1	146.2	404.3	101.0	4.2703	14,250
140.0	147.0	538.0	135.0	5.5990	14,440
140.0	147.0	538.0	135.0	5.5670	14,590
142.3	144.0	385.4	34.0	4.9780	14,555
142.3	144.0	385.4	24.0	4.9040	14,780
142.3	144.0	385.4	24.0	5.0515	14,350
142.4	142.4	370.6		5.0100	14,840
142.4	142.4	376.0		5.1325	14,695
142.4	142.4	398.1		5.5560	14,370
142.4	142.4	377.3	• •	5.1200	14,525
141.5	143.2	385.4	27.5	4.9309	14,555
141.3	143.3	395.4	32.6	4.8000	14,745
140.9	143.0	385.4	44.0	4.8080	14,240
140.5	143.1	365.6	48.0	4.3975	14,490
140.5	143.1	372.0	48.0	4.4960	14,455
139.5	143.0	381.1	40.2	4.8150	14,200
139.5	143.0	381 .1	40.2	4.8460	14,120

secutive determinations range from 14,140 to 14,840 calories. These variations are believed to be due almost entirely to accidental errors, such as variation in the heat loss and the amount of mercury that adhered to the vapor outlet tube. The latter error would tend to be eliminated by our method of sealing off successive bulbs one after the other, since if one contained less mercury, the next would probably contain an excess. No results were omitted in this series of determinations, and it can be

stated with some confidence that the arithmetical mean of the results obtained would not be changed appreciably by any number of additional determinations. The probable error calculated by the method of least squares is about 25 calories. Allowing a possible constant error of 25 calories in the calibration of the instruments, etc., the heat of vaporization of mercury is found to be $14,490 \pm 50$ calories at 142° C. If this value be corrected to 298° K. we obtain 14,670. The value obtained by differentiating the empirical equation of Smith and Menzies at 298° K. is 14,615 cal. While this close agreement cannot be assumed to prove the accuracy of our results it does, on the other hand, indicate a very high order of accuracy for the vapor-pressure data of Smith and Menzies, since a very slight error in vapor-pressure measurements would cause a much greater error in the calculation of heat of vaporization.

Heat of Vaporization of Cadmium

It would no doubt be possible to make a direct calorimetric determination of the heat of vaporization of cadmium using the same method that was employed in the case of mercury. It would be necessary, however, to work at a temperature of at least 350° where the effects of radiation would be very great and the experimental difficulties would probably be considerable. On the other hand, the results in the case of mercury indicate that heat of vaporization can be calculated with considerable accuracy from vapor-pressure data, and this is especially true in the case of cadmium because we have the very elaborate work of Wüst, Meuthen and Durrer⁹ on the specific heats of solid and liquid cadmium at high temperatures. By way of existing data on the vapor pressure of cadmium, there are only the measurements of Egerton¹⁰ on solid cadmium and a measurement of the boiling point of liquid cadmium by Heycock and Lamplough.¹¹

The simplest and most promising method for the measurement of the vapor pressure of a liquid at high temperatures appeared to us to be the measurement of the boiling point at various reduced pressures. This has been done, working over a range of pressures from about 10 mm. up to about 80 mm. with very satisfactory results. It was not possible to measure the pressures below 10 mm. with sufficient accuracy, and the measurements in the direction of higher pressures were limited by the softening point of Pyrex glass.

The apparatus used was modeled after that used by the Bureau of Standards¹² for determining the boiling point of sulfur. A sketch of the apparatus is shown in Fig. 2. The cadmium was boiled in a test-tube

⁹ Wüst, Meuthen and Durrer, "V. D. I. Forschungsarbeiten," 1918, p. 204.

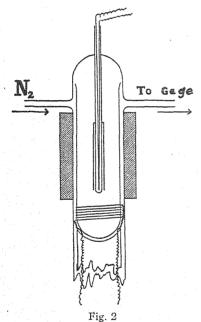
¹⁰ Egerton, Phil. Mag., 33, 33 (1917).

¹¹ Heycock and Lamplough, Proc. Chem. Soc., 28, 4 (1912).

¹² Bur. Standards Bull., **6**, 184 (1909).

25 cm. in depth by 3 cm. inside diameter, around the bottom of which a heating coil was wound. This tube was mounted inside of a larger tube that formed a closed system connected to a source of supply of nitrogen, and a gage and a pump. The gage was simply a U-tube manometer containing mercury, made from tubing about 2 cm. inside diameter. A vacuum of about 0.002 mm. was maintained in one limb of the manometer by a connection to an oil pump which was kept running while measurements were being made. A leveling bulb was connected to the bottom of the manometer so that the mercury levels could be raised or lowered.

The thermocouple was placed inside a glass tube, the lower end of which was about 3 cm. above the molten eadmium. Around the lower



portion of the thermocouple tube was placed an iron radiation shield which was designed to prevent molten cadmium from running down the thermocouple A platinum-platinumrhodium tube. thermocouple made by Heraeus was used, with a calibration chart furnished by the makers. This calibration was confirmed by checking the thermocouple against the boiling point of sulfur. The thermocouple e.m.f. was read upon a White potentiometer. The heights of the mercury in the manometer were read to 0.02 mm, with a cathetometer. Before each reading the mercury was moved up and down the manometer to free the meniscus and readings taken with the mercury at different heights in the manometer showed no variation due to unevenuess of bore. The outside tube for about 3 cm. above the heating

coil was uninsulated in order to prevent superheating as far as possible. Above this, the tube was covered with asbestos insulation to prevent too rapid cooling and condensation of the vapor around the thermocouple.

In the operation the tube was filled with nitrogen at the desired pressure and the cadmium boiled at such a rate that the vapor rose well above the radiation shield, the thermocouple being immersed about 10 cm. in the vapor. Experiment showed that the temperature did not change when the height of the vapor was changed by varying the heating current. When the temperature and pressure had become constant, two sets of readings were made with the mercury at different heights in the manometer. The first question that concerned us was whether the pressure as read by the

manometer is the same as that under which the vapor condenses on the thermocouple. This question is not easily answered because a very rapid current of vapor flows past the thermocouple when the cadmium is boiling. It is believed, however, that the average variation in pressure from that read by the manometer is negligible. The question of the accuracy of the temperature measurements is more serious. The thermocouple is not likely to be below the temperature of the vapor, but superheating can very readily take place. The first run was made with the cadmium meniscus about 3 mm. above the top of the heating coil. Results were obtained which when plotted with the logarithm of the pressure as ordinate and the reciprocal of the absolute temperature as abscissa gave a remarkably smooth curve that deviated but slightly from a straight line, as the theory would predict. It seems unlikely that any serious error in the temperature measurements could have occurred in this run, because a variation of even 1° in the temperature of an observation would cause noticeable deviation in the plot and if any considerable superheating were taking place it would have been very remarkable if noticeable irregularities in the data

TABLE II VAPOR PRESSURES OF CADMIUM

,		
Temperature ° K.	Pressure observed Mm.	Pressure calc. Mm.
594.1^{a}	0.10	0.10
-754.0	9.06	9.14
769.4	12.54	12.70
791.8	20.27	20.10
810.6	28.70	28.84
810.6	29.08	28.84
824.9	37.54	37.58
827.5	39.23	39.45
837.5	47.29	46.99
846.3	54.60	54.95
853.2	61.24	61.66
867.6 .	78.04	78.34
1039.0^{b}	760.00	785.2

[&]quot; Egerton.

had not appeared. A second run was made with the cadmium surface about 3 cm. above the heating coil. No satisfactory observations were obtained in this run because of the violent bumping and unsteady boiling. A third run was made with the cadmium slightly below the top of the heating coil; in this case, superheating evidently took place and the results when plotted gave a very irregular curve. A fourth run was made with the cadmium surface about 1 cm. above the top of the heating coil, and the results obtained at lower pressures checked very closely the results of the first run. At higher pressures the cadmium began to bump

b Heycock and Lamplough.

and the observations again became uncertain. When the cadmium surface was slightly above the heating coil the boiling was very smooth and the temperature as read by the thermocouple was very constant and responded at once to the slightest change in pressure. It is believed that the temperatures observed under these conditions are not in error by more than 0.5° .

Eleven observations are given in Table II, each observation being the mean of two separate readings taken at the same pressure. The cadmium used was of very high purity.

We should be unable to do better than give a rough approximation of the heat of vaporization of cadmium were it not for the previously mentioned work of Wüst, Meuthen and Durrer⁹ on the specific heat of liquid cadmium. If we use their equation for the specific heat of the liquid and assume $C_p = 4.97$ for the vapor, we then have for the heat of vaporization of liquid cadmium

$$\Delta H = \Delta H_0 - 2.453 \ T - 0.000716 \ T^2 \tag{2}$$

Substituting this in the Clapeyron equation (1) and integrating, we have

$$\ln p = -\frac{\Delta H_0}{RT} - \frac{2.453 \ln T}{R} - \frac{0.000716}{R} T + C$$
 (3)

We thus have only ΔH_0 and C to determine.

The value for the vapor pressure at the melting point determined by Egerton¹⁰ is presumably not of high accuracy. Nevertheless, we shall find that it agrees very well with our determinations. The value for the boiling point obtained by Heycock and Lamplough¹¹ may likewise be in error by 2° or 3°. Furthermore, we can scarcely expect our equation to be strictly applicable at pressures of 1 atmosphere unless cadmium vapor is very nearly an ideal gas in its behavior. Hence, we shall be satisfied if our vapor-pressure equation approximates the value of Heycock and Lamplough. Accordingly, we find that if we assume $\Delta H_0 = 27,060$ cal. and take Egerton's value at the melting point as valid we obtain the final equation for vapor pressure in this form,

$$\log p_{\text{(mm.)}} = -\frac{5910}{T} - 1.234 \log T - 0.000156 T + 12.467 \tag{4}$$

This equation gives excellent agreement with the data and leads to a value for ΔH at 594.1° K. of 25,350 cal. It is believed that the data are not likely to be in error by enough to change the value for ΔH by more than 100 cal.

The Entropy of Monatomic Vapors

We are now in a position to calculate with considerable accuracy the entropy of mercury and cadmium vapors at 298° K. and 1 atmosphere. In the case of mercury the only change that we shall make from the calculation of Lewis, Gibson and Latimer³ is in the slightly greater heat of

vaporization. In the case of cadmium, the specific-heat data of Rodebush¹³ indicate an entropy of 11.97 for solid cadmium at 298.1° K. The data of Wüst, Meuthen and Durrer⁹ on specific heats and heat of fusion and our determinations of vapor pressure enable us to calculate the entropy of the vapor. Sackur, Tetrode, and others² have predicted that the entropies of the different monatomic gases at 298.1° K. and 1 atmosphere would be represented by the equation, $S = 3/2 R \ln M + C$, where M is the atomic weight and C a constant. Lewis has predicted that the constant would have a value of 25.70. The values we obtained are tabulated together with Lewis's theoretical calculations.

TABLE IV

The equation of Rodebush¹⁴ appears to fit the data for mercury and

$$p = \frac{\mathbf{N}RT}{N^2H} \sqrt{2 M \Delta H_0} \ e^{-\frac{\Lambda H_0}{RT}}$$

cadmium remarkably well. It is apparent that we can calculate a very good value of heat of vaporization provided we have only a very rough value for the vapor pressure at one temperature. Thus, for mercury at 298.1° K., we calculate $\Delta H_0 = 14,800$ cal. as against 14,670 found experimentally. For cadmium at its melting point we find $\Delta H_0 = 25,750$ cal. as compared with the experimental value, 25,350. The extraordinarily high specific heat of molten cadmium indicates that a greater deviation between ΔH_0 and ΔH may be expected than in the case of mercury.

From Egerton's value of 1.13 mm. for the vapor pressure of zinc at the melting point we may calculate the heat of vaporization of molten zinc. The value we obtain, 26,800 cal., we may expect to be somewhat high, as in the case of cadmium. We can check this by calculating the entropy of zinc vapor at 298.1° K. and 1 atmosphere, since we have all the necessary data. The result is somewhat high as may be expected, 39.1 entropy units, as compared with a predicted value of 38.2. This is a further confirmation, if any be needed, of the experimental generalizations that suggested the work of this paper.

¹³ Rodebush, This Journal, 45, 1413 (1923).

¹⁴ Here N is the number of molecules per sq. cm. of liquid surface, N is Avogadro's number, h is Planck's constant, M is the molecular weight, and $\Delta H_0 = \Delta E_0 + RT$ where ΔE_0 is the work necessary to remove a molecule from the surface of the liquid which is not in general the same as ΔE , the internal energy of vaporization. In the derivation of this equation (Reference 5) ΔE_0 was assumed to be identical with ΔE , ΔH_0 will usually be larger than ΔH .

Summary

The value of directly measured heat data as a supplement to vaporpressure data is pointed out.

The heat of vaporization of mercury is determined calorimetrically to be 14.670 ± 50 cal. at 298.1° K.

The heat of vaporization of cadmium is found to be $25,350 \pm 100$ cal. at 594.1° K.

The generalizations regarding the entropies of monatomic gases and relating vapor pressures to heats of vaporization are confirmed for zinc, cadmium and mercury.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE ACTION OF SELENIUM OXYCHLORIDE ON VARIOUS METALS AND METALLIC OXIDES¹

By WARD L. RAY Received June 18, 1923

In his studies of selenium oxychloride, Lenher² has shown that this inorganic solvent reacts with most of the metals to give the chloride of the metal and selenium monochloride; also that many of the metallic oxides are dissolved by selenium oxychloride.

The object of this research was to study these actions in greater detail and to extend the study, in certain cases, to the action of selenium oxychloride on some closely related substances such as the selenides and the selenites.

The temperatures at which the reactions take place have been varied between room temperature, that of a steam-bath (about 90°), and in some cases the boiling point of selenium oxychoride (175°). A few reactions were studied at even higher temperatures.

Manipulation

About 10 cc. of selenium oxychloride, prepared by the interaction of selenium dioxide and selenium tetrachloride and purified by vacuum distillation,³ and from 0.2 to 0.5 g. of the metal of oxide were placed in tubes and sealed, to avoid the access of moisture and the consequent hydrolysis. These sealed tubes were allowed to stand at room temperature or were heated on the steam-bath until reaction was complete, or had progressed sufficiently far for our purposes. In some cases a day was required, in others a year.

¹ Abstract of a part of the thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

² Lenher, This Journal, 43, 29 (1921).

² Lenher, ibid., 42, 2498 (1920).

In the experiments at the boiling point of the selenium oxychloride, the reactants were gently boiled either in small Erlenmeyer flasks or in glass tubes closed with watch glasses, and heated on a sand-bath or an electric hot-plate.

Analytical Procedure

In analyzing the precipitates formed in the various reactions it was necessary to use a non-aqueous solvent to wash out the excess of selenium oxychloride, and selenium monochloride when any was formed. The solvents found most satisfactory were carbon tetrachloride and chloroform.

The general method used to prepare the precipitates for analysis was to pour the selenium oxychloride containing the precipitate into a large excess of chloroform. The precipitate was washed several times by decantation, given a final washing on a filter paper or Gooch crucible, and dried in an air oven at 115° or in a special electrical drying apparatus in a current of dry air, depending upon whether it was easily hydrolyzed by the moisture of the air.

Selenium.—Selenium was determined gravimetrically as elementary selenium. It was precipitated from a hot, 15% hydrochloric acid solution, with a saturated solution of sulfur dioxide.

Selenium Monochloride.—Selenium monochloride reacts with water according to the following equation.

$$2Se_{2}Cl_{2} + 3H_{2}O = 4HCl + H_{2}SeO_{3} + 3Se$$
 (1)

The weight of the selenium precipitated is used to calculate the amount of monochloride that may be dissolved in selenium oxychloride, as the action of water on the selenium oxychloride gives selenious and hydrochloric acids.

Chlorine.—Chlorine was determined gravimetrically as silver chloride, sufficient nitric acid being used to prevent the precipitation of silver selenite.

Metals.—The general method of analyzing the residues obtained from the action of selenium oxychloride on the various metals and their oxides was to use one sample for the determination of chlorine and another for the determination of selenium. The filtrate from the selenium determination was evaporated to dryness and the metal in this residue determined by the most convenient method.

Experimental Part

Copper.—When selenium oxychloride is added to sheet copper at room temperature, the metal gradually becomes covered with a black substance which analysis indicates to be a mixture of cuprous and cupric selenides, Cu₂Se and CuSe. This black coating is gradually changed into anhydrous

cupric chloride. Selenium dioxide and selenium monochloride are formed at the same time. The completed reaction might be expressed as follows.

$$3Cu + 4SeOCl2 = 3CuCl2 + 2SeO2 + Se2Cl2$$
 (2)

The determination of the amount of selenium monochloride formed when a definite amount of copper is acted on by selenium oxychloride substantiates Equation 2.

Cuprous selenide, prepared by heating copper and selenium to 600°, reacts with selenium oxychloride to give cupric chloride, selenium monochloride and selenium dioxide.

A New Selenite of Copper.—When selenium oxychloride and anhydrous cupric chloride are heated together in contact with the air, a green crystalline salt is formed. Analysis shows this salt to be an acid selenite of copper, CuSeO₃.SeO₂, which has not hitherto been reported. Various experiments indicate that the formation of the salt is as follows.

$$CuCl_2 + 3SeO_2 = CuSeO_3.SeO_2 + SeOCl_2$$
 (3)

The selenium oxychloride simply acts as a solvent for cupric chloride and selenium dioxide. Selenium dioxide formed by the hydrolysis of some of the selenium oxychloride by moisture of the air is dissolved in the excess of selenium oxychloride, and when a certain concentration of selenium dioxide is reached the copper selenite is formed. The reaction may be made to go from right to left by adding selenium oxychloride that is not saturated with selenium dioxide.

Anhydrous cupric chloride and selenium dioxide heated together give selenium oxychloride and a selenite of copper.

Oxides of Copper.—Selenium oxychloride slowly reacts with cupric oxide to form cupric chloride and selenium dioxide according to the following equation.

$$CuO + SeOCl2 = CuCl2 + SeO2$$
 (4)

Cuprous oxide heated with selenium oxychloride is oxidized to cupric chloride, while a part of the selenium oxychloride is reduced to selenium monochloride.

CuSeO₃.2H₂O.—Selenium oxychloride reacts at once with cupric selenite CuSeO₃.2H₂O to give anhydrous cupric chloride. Many other copper salts were treated with selenium oxychloride, and in every case anhydrous cupric chloride was formed. The reaction may be expressed as follows.

$$CuSeO_3.2H_2O + 3SeOCl_2 = CuCl_2 + 4SeO_2 + 4HCl$$
 (5)

Silver.—Selenium oxychloride acts very slowly on sheet silver, yet the reaction is similar to that between selenium oxychloride and copper. Black silver selenide, Ag₂Se, which is later changed into silver chloride, is first formed, or at least is formed in such quantities as to mask the silver chloride that may be formed simultaneously. Both the silver selenide and the silver chloride form a coherent film on the silver, and this retards

further action. Silver selenide, prepared by heating precipitated silver with an excess of selenium at red heat for 20 minutes, reacts slowly with selenium oxychloride to give silver chloride.

Precipitated silver is rapidly changed into silver chloride when carefully added to cold selenium oxychloride. Silver leaf added to cold selenium oxychloride turns black at once, and in less than a minute is changed into a sheet of gelatinous silver chloride that floats on top of the selenium oxychloride. If the selenium oxychloride be hot, the reaction is similar, except that the film of silver chloride is thicker.

Silver Oxide.—Selenium oxychloride and silver oxide react with the evolution of light and heat to give selenium dioxide and silver chloride. The heat of the reaction decomposes a part of the silver oxide.

Lead.—Selenium oxychloride reacts more rapidly with lead than with either copper or silver. There is no indication that lead selenide is formed as an intermediate compound. The lead chloride that is formed is granular and drops away from the metal, thus exposing fresh surfaces to the action of the selenium oxychloride.

The Oxides of Lead.—When selenium oxychloride in small amounts is added to lead oxide, red lead and lead dioxide, the reaction is accompanied by the evolution of heat and light. With the last two oxides chlorine is evolved. The following equation represents the action of selenium oxychloride on lead dioxide.

$$PbO_2 + 2SeOCl_2 = PbCl_2 + 2SeO_2 + Cl_2$$
 (6)

Nickel and Cobalt.—Nickel and cobalt are very slowly attacked by selenium oxychloride. These metals in sheet form were placed with selenium oxychloride in sealed tubes and allowed to remain at room temperature for over a year. The selenium oxychloride was slightly darkened by selenium monochloride, while a small amount of the metallic chloride was in the bottom of each tube. The reaction between selenium oxychloride and the finely divided metals is more rapid.

The oxides of these metals slowly react with selenium oxychloride to give the metallic chloride and selenium dioxide.

Iron.—The chlorides of the metals so far discussed are either insoluble, or only slightly soluble, in selenium oxychloride. Thus, when the metal is added to a large excess of selenium oxychloride, the selenium monochloride and the selenium dioxide formed during the reaction are dissolved in the excess of selenium oxychloride, while the metallic chloride separates. A number of other metallic chlorides are more soluble in selenium oxychloride.

Iron dissolves rapidly in hot selenium oxychloride. The ferric chloride formed during the reaction remains in solution, but some of it is precipitated when the solution is repeatedly heated and cooled. In the cold, the reaction is slow and most of the ferric chloride separates from solution as fast as formed.

Ferric oxide is only slowly affected by selenium oxychloride at room temperature, but when selenium oxychloride in the vapor state is passed over ferric oxide heated to 400°, the reaction is rapid. Ferric chloride and selenium dioxide collect on the cooler portions of the tube.

Antimony and Bismuth.—These metals treated with a large excess of selenium oxychloride dissolve completely. A study of the amount of selenium monochloride formed during the reactions shows that bismuth is oxidized to the trichloride. The amount of selenium monochloride formed when antimony is dissolved in selenium oxychloride is more than would be formed to oxidize the antimony to the trichloride, but not enough to oxidize it to the pentachloride.

Tin.—When tin is added to cold selenium oxychloride, action begins at once. The selenium oxychloride becomes dark red from the selenium monochloride formed during the reaction. No precipitate is formed. When sufficient tin is present, the reaction continues until the solution becomes so viscous that it will not run from one end of the tube to the other. The tin is oxidized to stannic chloride.

It was not possible to prepare Weber's⁴ compound, SnCl₄.2SeOCl₂, from the action of selenium oxychloride on tin. The presence of selenium dioxide and selenium monochloride dissolved in selenium oxychloride evidently prevents the reaction between the latter and stannic chloride to form SnCl₄.2SeOCl₂.

The author wishes to acknowledge his appreciation of the inspiration and helpful suggestions received from Professor Victor Lenher, under whose direction this work was carried out.

Summary

- 1. A detailed study has been made of the action of selenium oxychloride on 9 metals, 9 metallic oxides, and 2 selenides.
 - 2. A new selenite of copper has been prepared.

Madison, Wisconsin

⁴ Weber, Pogg. Ann., 125, 135 (1865).

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

A METHOD FOR PHOTOGRAPHING THE DISINTEGRATION OF AN ATOM, AND A NEW TYPE OF RAYS¹

By WILLIAM D. HARKINS AND R. W. RYAN

Received June 25, 1923

Introduction

In 1915 Harkins and Wilson² published the first definite theory of the composition of the nuclei of atoms in terms of hydrogen and helium. The theory predicted a general difference of stability between the atoms of elements of even and those of odd atomic number. That this prediction is definitely confirmed was shown in a later paper,³ where it was demonstrated that (1) the elements of even atomic number are represented in the meteorites by 70 times as many atoms as those of odd number; (2) every one of the 7 most abundant elements in the meteorites has an even atomic number; (3) every one of the 5 undiscovered elements has an odd atomic number, and (4) there are many more atomic species (isotopes) of even than of odd atomic number.⁴

An altogether different type of confirmation was supplied later by Rutherford.⁵ He was able to disintegrate atoms of the elements 5, 7, 9, 11, 13 and 15, in such a way that they give off hydrogen in every case, while he did not obtain any evidence that atoms of elements of even atomic number disintegrate at all. Now, the theory of Harkins specifically pointed out that the energy of combination of hydrogen to form helium is so great that a disintegration of any atom built up entirely of helium would probably in no case give hydrogen (Table I), but it indicated that elements of odd atomic number contain hydrogen not combined into

¹ Presented at the Intersectional Meeting of the American Chemical Society, Urbana, Ill., May 4, 1923.

Parts of this paper have been presented or photographs of α -ray tracks have been exhibited at the following meetings: American Chemical Society, Pittsburgh, September, 1922; American Physical Society, Chicago, November, 1922; Washington, April, 1923; Section C., A. A. A. S., Boston, December, 1922. Letters concerning the work, with photographs, have been published in *Nature*, 111, 27 (Jan.), 1923, and 112, 54 (July), 1923.

Presented by R. W. Ryan as a thesis in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

- ² Harkins and Wilson, *Proc. Nat. Acad. Sci.*, **1**, 276 (1915). This Journal, **37**, 1367 (1915).
 - 3 Harkins, This Journal, 39, 856 (1917).
- ⁴ That this follows from the theory of Harkins was shown by N. F. Hall [*Ibid.*, 39, 1606 (1917)].
- ⁵ Rutherford, *Phil. Mag.*, **37**, 538 (1919). Rutherford and Chadwick, *ibid.*, **42**, 809 (1921).

helium, and these would thus be capable of disintegration to give hydrogen, as accords with the experimental results.

TABLE I ENERGY OF ALPHA-PARTICLES

Energy of formation of 1 g.-atom of helium from 4 g.-atoms of hydrogen = -2.8×10^{19} ergs. (-4.6×10^{-5} ergs per atom of He)

Source of α-particle	Velocity	Kinetic Per particle × 10 ⁵	energy, Per gram atom \times 10 $^{-18}$
Po	0.0523 c	0.812	4.92
Ra C'	.0641	1.218	7.38
Th C	.0572	0.970	5.88
Th C'	.0688	1.404	8.51

The table indicates that the highest kinetic energy for any of the α -particles listed is less than 1/2 the energy of formation of an α -particle from protons and electrons. "c" is the velocity of light.

The scintillation method as used in these experiments by Rutherford, is capable of detecting disintegration particles which have only a range greater than 30 cm. in air, since hydrogen atoms which are merely released from chemical combination in water, hydrogen, and other compounds, have nearly this range, while H+ particles (protons) released from the nucleus of an atom have a greater range. In the case of the aluminum nucleus, for example, it is 90 cm. However, other disintegrations may occur. Thus, when bombarded by swift α -particles, certain atom nuclei may give disintegration fragments, such as α -particles, H⁺ particles, or electrons, of a shorter range than 30 cm. Since all such particles, of any range down to less than a millimeter, leave visible tracks in the ray track apparatus of C. T. R. Wilson,7 it would seem that a method could be devised which would utilize this apparatus for the detection and study of nuclear disintegrations induced by the impact of swift α -particles, provided the characteristics which such a disintegration would exhibit could be determined, and to do this is very simple.

Photographs of Atomic Collisions. (Collisions of the Nuclei of Atoms)

In order to disintegrate an atom nucleus artificially it is necessary to bombard it with a high-speed helium nucleus (α -particle).⁸ The scintillation experiments of Rutherford,⁹ and of Geiger and Marsden¹⁰ have shown that the α -particle must pass through an extremely great number of atoms

- 6 In the 1915 paper from this Laboratory it was pointed out that the packing effect for hydrogen nuclei in a complex nucleus is smaller in all probability when the hydrogen is not combined in an α -particle. The atomic weight of nitrogen, 14.01, indicates that this is true in the nitrogen nucleus unless the 0.01 in excess over a whole number is due to experimental error.
 - 7 Wilson, Proc. Roy. Soc., 87, 277 (1912).
 - 8 It is of course possible that high-speed electrons may also induce disintegration.
 - ⁹ Rutherford, Phil. Mag., 21, 669 (1911).
 - 10 Geiger and Marsden, Proc. Roy. Soc., 82A, 495 (1909).

in order to secure a single collision with the nucleus of an atom, and the photographs described in the present paper demonstrate this in a much more direct way.

The writers have taken 21,000 photographs of α -ray tracks in air and a few in helium and ethyl chloride. Of these 10,000 were secured by using polonium, and 11,000 by using thorium C and C' as the source of the α -particles. In all, about 80,000 tracks have been photographed. In each of these the α -particle passes directly through between 100,000 and 200,000 atoms, provided atoms have the dimensions usually attributed to them. In all about 12 billion atoms have been shot through, with the remarkable result that in only 3 cases has the nucleus of an atom of the

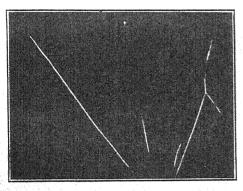


Fig. 1.—Sharp atomic collision with a visible track of the bombarded nitrogen or oxygen nucleus. The fork exhibits conservation of momentum which proves that the nucleus remains stable under the impact

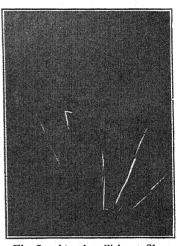


Fig. 2.—Atomic collision. Shows an apparent but not a real, contradiction of the principle of conservation of momentum

gas been hit sharply enough to give a retrograde motion to the α -particle after the collision. Thus for each sharp collision the α -particles have had to shoot through about 4 billion atoms. This fact taken alone would indicate that the radius of the nucleus of an atom of air¹¹ is of the order of $\frac{1}{30,000}$ that of the atom, which would give the nucleus a radius of the

order of a little more than 10^{-13} cm. Since the number of hits is so small, a closer estimate could be secured by a consideration of the numerous cases in which the particle is slightly deflected from its path by the repulsion between its positive charge¹² of 2 and that of 7 on the nitrogen nucleus.

Fig. 1 gives a reproduction of a photograph of the sharpest nuclear

¹¹ An atom of nitrogen or oxygen.

¹² In this paper the charge on the electron is taken as of unit magnitude.

collision ever obtained, with one exception. The α -particle from a polonium source, with an initial velocity of 1.357×10^{10} cm. per second, is turned through an angle of 155° and rebounds for a distance whose horizontal projection is about 5.2 mm. while the nitrogen nucleus is projected forward for a corresponding distance of 3.8 mm. If the track of this

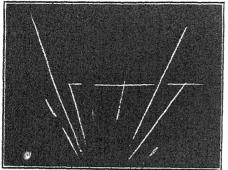


Fig. 3.—Effect of old tracks in the taking up of water vapor

nucleus is projected backward it may be seen that the line thus obtained lies slightly closer to the track of the on-coming, than to that of the retreating α -particle. This is essential in order that the impact shall exhibit conservation of momentum, since the α-particle has much less momentum after the collision than it had before.

The characteristics of an ordinary collision are: (1) the initial track splits into two branches,that is, three lines converge at

one point in space, -(2) momentum is conserved in the collision and (3) the three tracks lie in one plane. In addition, energy is conserved.

provided the presumably small amount of energy radiated is taken into account.

Fig. 2 shows the third sharpest collision photographed, and is presented as an example of an apparent, but not a real, contradiction to the principle of conservation of momentum in an impact. Here the track of the bombarded nucleus does not appear in the photograph. Presumably this is due to a lack of water vapor for the production of the track. This showing old track threading the loop often occurs and is due to a con-

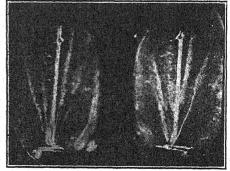


Fig. 4.—Loop formed by two α-ray tracks,

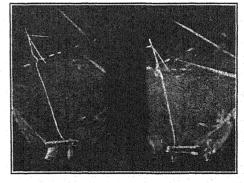
version of the water vapor in a particular region into the minute drops which form a track. These drops are electrically charged and are drawn out of the gas by an electrical field of 500 volts per cm. If a second track passes through this region within a few tenths of a second there is not sufficient moisture to enable water to gather in drops on the ions, so there appears to be a break in the track. In one photograph (Fig. 3) there are two such breaks in a transverse track; one due to a track which has passed so recently that it appears very sharp, while the other is caused by an older track which has become diffuse and has been mostly swept out by the electric field. The transverse track was photographed almost immediately after its formation. If it had remained slightly longer, ions produced by the α -particle would have diffused out (or have been pulled out by the field) of the dry region into a space which contains more moisture, and here an apparent loop somewhat like half of an ellipse cut along its longer axis would have appeared in the track. This bends either upward or downward corresponding to whether the new track lies above or below the old one. In some cases it bends in both directions, and the remnant of the old track is photographed as if threading the eye of a needle. (Fig. 4.)

Characteristics Exhibited by a Photograph of the Disintegration of an

In order to secure the transfer of a large amount of energy to the nucleus to be disintegrated, the incident α -particle should have as high a speed as is possible, and also the collision should be as sharp as can be obtained. The former of these conditions was met in the experiments under discussion in this section, by the use of thorium C and C' as a source. Fig. 5 shows the sharpest collision ever photographed. The angle in space

between the lines representing the tracks of the α -particle is only 15°, so that the particle has been turned through an angle of 165°.

Where a nuclear collision occurs, the initial track splits into two branches. If it should split into three branches, one of these would be due to the rebounding α -particle, one to the forward path of the nucleus which is hit, and a third track, provided it were due to a positively charged nucleus, would indicate a par-



and a third track, provided it Fig. 5.—Sharpest collision of atomic nuclei were due to a positively charged photographed. Shows the number of tracks characteristic of an atomic disintegration

ticle torn off from the bombarded nucleus by a process of disintegration. Now it happens that the tracks of positively charged nuclei are usually easily distinguished from those of negative electrons, since the latter are much fainter, and more highly curved. It might seem that the extra track was caused by the collision of the α -particle with a second nucleus which is not very distant from the first one, but nuclear collisions are so rare that this

is extremely improbable. Even if it should occur, the momentum and energy relations are such as to give a type of double fork which could probably be recognized. Thus, the energy imparted to the nuclei would be taken from that of the α -particle, so the latter should have a shorter range if it gives energy to a second nucleus than if it hits only one. The energy difference can be estimated, within rather wide limits, from the range of the nuclei that are hit. Even at such high speeds as those used in this work there should be no considerable departure from the principle of conservation of momentum in the combined impact and disintegration. Therefore, whenever all of the tracks show, the photograph should exhibit this conservation. However, Fig. 2 demonstrates that the track of even a highly charged positive nucleus may fail to appear. From this point of view it would not seem strange if the faint tracks due to high speed electrons or H $^+$ particles should remain invisible.

If a disintegration should occur, the α -particle and the bombarded nucleus alone would not be expected to exhibit conservation of momentum, though momentum is always conserved in a collision unaccompanied by a disintegration. This indicates that if the tracks of these particles as shown by the photograph are such that momentum is not conserved for the two particles alone, and atomic disintegration has taken place.

In a simple collision it is to be expected that all of the tracks should lie in a plane. If a disintegration occurs this should not be true except by accident.

Fig. 5 shows an α-ray track which splits into 3 branches after the collision occurs, so it has this characteristic to be expected if the bombarded nucleus disintegrates. The extra track is too bright to be caused by an electron, though its extreme brightness is due to the fact that it is photographed almost "head-on." It is evident that the visible tracks do not exhibit conservation of momentum, which may indicate that other particles are emitted at the same time, but do not show. The tracks in the original negative are sharp—much sharper than in the reproduction, and a study of the film under the microscope seems to show that if the third particle is neglected, the remaining tracks do not show conservation of momentum as they should if the collision is a simple one. The question arises, could the extra track have been formed by the disintegration of a radioactive particle exactly at the point of collision at almost exactly the time of the collision? It cannot be stated that this is an absolute impossibility, but it is certain that the probability of such a coincidence is excessively small. At any rate the method used in these experiments will in general photograph atomic disintegrations if they occur.

Zeta (¿) Rays

Delta(δ)-rays were first found in gases by Bumstead, who gave them a sufficient range for observation by causing them to appear in hydrogen

at low pressures. The rays are given off at nearly right angles to the track of the α -ray which produces them. They are very short in air at ordinary pressure, not more than 0.5 mm. in length, and end in a knob which is easily visible. It is supposed that they are produced by low speed electrons removed from the atoms by the passage of the particle.

C. T. R. Wilson has secured beautiful photographs of these rays, and the writers have often observed them, particularly in helium.

Fig. 6 shows a new type of rays, which may be called zeta (t) rays. Their range is very many times greater than that of the δ -rays. They are much rarer, and give faint, but very definite tracks. Their faintness and high curvature makes it seem probable that they are Probably due to electrons due to electrons torn out of the

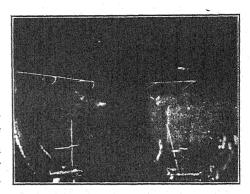


Fig. 6.—Rays of a new type (Zeta Rays).

atoms, possibly from the K level. The figure indicates that the ejection of the first ζ -ray does not materially change the direction of the α -ray track, and this, taken in connection with the length of the tracks shows that the mass of these particles must be low, as would be the case if they are electrons.

These rays present features of extreme interest.¹³ Thus in Fig. 6 the

¹⁸ In a letter in Nature, 111, 463 (April 7, 1923), Bose and Ghosh present three interesting photographs of α -ray tracks in helium. The interpretation of these photographs is difficult, since only one projection was obtained, but it seems that electrons have been ejected from helium atoms by the passage near or through them of α -particles. In this respect there is some similarity to what has been discussed above under the designation of ζ-rays. However, their rays possess quite different characteristics, since they are not projected backward. In order to determine the nature of the rays secured by them two projections should be obtained, since one projection may reveal entirely different characteristics from those exhibited by the other.

Their photographs do not resemble those which depict the collision of 2 atom nuclei, since in each case there seems to be a continuation in a straight line of the initial α -ray track beyond the point where the branching occurs.

Since the nucleus of the argon atom is larger, and the electric field around it is also stronger, than for nitrogen or oxygen, it is much easier to secure photographs of atomic collisions in argon than in either of the two other gases. Blackett [Proc. Roy. Soc., 103A, 62 (1923)] obtained one collision in which the α-particle from polonium was turned through an angle of about 110°, but this is much less sharp than those given in Fig. 1 (125°) and in Fig. 3 (165°).

In addition to the 21,000 photographs of α -ray tracks in air described in the body of the paper, the writers have now obtained about 20,000 photographs of tracks in argon.

2 ray-tracks are practically parallel. Both start upward and give curves that are convex upward. The particles have a considerable retrograde motion, and their range is about 3 mm.

Of these, two are so remarkable that they are presented in Figs. 7 and 8. One of these, Fig. 7, represents by far the most remarkable simple collision yet obtained, in that the

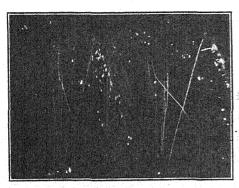


Fig. 7.—Collision of fast α -particle with the nucleus of an argon atom. The hardest hit thus far photographed. The fork exhibits conservation of momentum, which proves that the argon nucleus has not disintegrated

speed of the a-particle is far higher than for any previous case. even after the loss of a considerable fraction of its energy by collision with an argon nucleus, the velocity of the rebounding α -particle is nearly 1/20 that of light, or 18,000 times that of the fastest rifle bullet. The range of the argon nucleus in argon is very high, about 8 or 9 mm. under the conditions of the experiment. The most remarkable feature of this photograph is that it shows that even under this terrific impact the argon nucleus remains intact, so its stability must be of an extremely high order. The α -particle in question has its source in thorium C'. so its initial velocity is 0.688 c.

A nuclear collision which is not simple is represented in Fig. 8. An

 α -particle from a source consisting of thorium C and thorium C' strikes an argon nucleus and is deflected diagonally upward through more than 45°. Two other tracks

spring from the point of collision, as is made evident by the two projections which go more or less downward. As nearly as can be told, there is a total conservation of momentum in the im-The appearance of the two tracks for the bombardment nucleus instead of one indicates that (1) the argon nucleus disintegrates, or (2) the bombarded argon nucleus collides with a second argon nucleus within 0.5 mm. of its starting point. There is a third possibility, that the α -particle hits 2 argon nuclei in direct succession, but the probability of such an occurrence is almost negligible. The angle between the two tracks under discussion is about 80°. From the 20,000 photographs of α -ray tracks in argon, and by a consideration of the stopping power of argon,

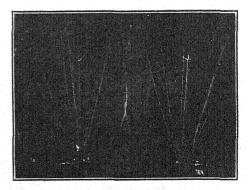


Fig. 8.—Double collision of atom nuclei in argon. The α -particle collides with the nucleus of an argon atom, and probably this in turn collides with a second argon nucleus. Both views of the collision are clear in the original photographs

it has been calculated that the probability that an argon nucleus will hit a second argon nucleus within a distance of 0.5 mm. in such a way as to give an angle as great as 80° between them, is small, possibly about 1 in 1000, the most uncertain factor being that

Experimental Part

The apparatus used is shown in Figs. 9, 10, and 11.

It is essentially a modified Shimizu-Wilson apparatus, 14 and consists of a glass cloud chamber N (Fig. 9) fitted with a piston and provided with a means for securing a sudden expansion. The roof of this cloud chamber is a glass plate K coated underneath with moist gelatin to which copper sulfate has been added. The top of the piston is also coated with moist gelatin blackened with india ink (not waterproof). A source of α -rays is provided at one side of the chamber as shown in Fig. 11 (B). Electrons given off and ions formed by the passage of α -particles through a gas serve as nuclei for the formation of water drops during the expansion and consequent cooling of the nearly saturated gas. A motion picture camera A is provided with a driving mechanism and an optical system such as to take views at right angles at the end of each expansion.

The most important modifications of the original Shimizu-Wilson Apparatus and the method of securing the rays are: (1) the use of a standard

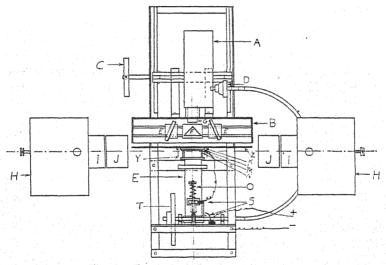


Fig. 9.—Front view of ray track apparatus

motion picture camera driven by a flexible shaft (A, Figs. 9 and 10); (2) a special cam R (Fig. 10) used to secure a sudden expansion (a related to the speed of the argon nucleus. Nevertheless, the characteristics of the tracks around the point of impact suggest that this double collision is probably what has occurred. The shortness of the two tracks, and their approximate equality in length seem to point to the conclusion that in this case a disintegration has not occurred. That the two short prongs are not due to electrons is indicated by the fact that the α -particle is deflected too sharply to give conservation of momentum with such light particles. Thus it seems probable that Fig. 8 represents the first "double collision" of atom nuclei to be photographed, though the possibility that the argon nucleus has disintegrated is not at all excluded. (Received August 9, 1923.)

¹⁴ Shimizu, Proc. Roy. Soc. (London), 99A, 425 (1921).

somewhat similar device is used by Blackett¹⁵); (3) the use of ThC, ThC', and RaC as source of α -rays; (4) the electric field used to sweep out water drops between the expansions is applied by means of brush con-

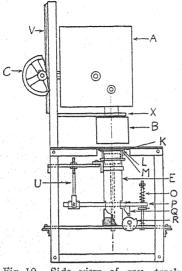


Fig. 10.—Side view of ray trac apparatus

tacts S instead of by a commutator; (5) a variable voltage transformer and a 500 volt kenotron (with a 1mf. condenser) is used as a source of this field; (6) the use of a moving screen prevents α -particles from entering the chamber except during maximum expansion.

The cylinder of the cloud chamber was ground from a well annealed borosilicate glass blank so as to give the uniform small clearance necessary to secure good cloud tracks. A capillary stopcock was provided on one side so that various gases might be introduced. Fig. 11 shows the means of screening α-particles from the chamber except at maximum expansion. A is a copper strip used as a screen to track prevent rays from entering the chamber except at the time of maximum expansion

and B is a Bakelite block holding the copper wire carrying the active deposit. This is so bored that α -particles are able to shoot out in only

a narrow beam; α -particles shot out at other times than at maximum expansion give diffuse tracks.

ThC and ThC' served as the source of the α -particles for much of this work. About 1 mg. of radiothorium is first dissolved in concd. hydrochloric acid. Then a copper wire is coated with wax, except at one end, and immersed in this solution for about half an hour or longer if the solution is weaker. The "active deposit" of thorium, consisting largely of ThC and ThC', deposits (by displacement) on the exposed copper. The end of the wire is then cut off and placed at

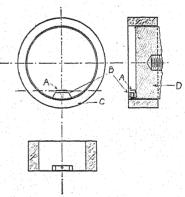


Fig. 11.—Diagram of ionization chamber

the base of the Bakelite block (B, Fig. 11). The very short life of ThC (only a few hours) makes it necessary to prepare this source immediately before use. Polonium sources are prepared in a similar way from solu-

¹⁵ Blackett, Proc. Roy. Soc., 102A, 294 (1922).

tions of RaF in hydrochloric acid but have a life measured in months instead of hours.

The photographic equipment includes a motion picture camera (A, Fig. 9) driven by a flexible shaft which carries a clutch D and thus allows the timing of the shutter with the expansion. This camera is provided with a Taylor-Hobson-Cooke F/2 lens in a focusing mount G, and an optical system which consists of two adjustable surface silvered mirrors E, and a prism F. These mirrors are carried on a 3-point support that slides along a track shown in Fig. 9, while the prism is clamped directly below the lens.

The cloud chamber is illuminated by two d. c. right-angle arcs, each provided with an 11cm. aspheric condenser and a cooling cell. Ammeters are used in both circuits and the current is adjusted so as to afford uniform illumination. Slits are provided on the cooling cell J and at Y in order to prevent the beam of light from striking the lower surface of the glass roof of the cloud chamber or the top of the piston at the moment of expansion.

In both views parts of the frame, the driving apparatus, etc., have been left out so that a clearer view of the essential parts of the apparatus could be given.

For a successful photograph a very sharp expansion is necessary, so that a fairly heavy spring O is used to force down the piston immediately upon its release by the cam R (Fig. 10). Means are provided for varying the length and the height of the stroke at U, and a locknut just below P regulates the expansion ratio. Somewhat exact adjustment is required to give the optimum conditions. A monatomic gas such as helium or argon requires a small expansion to secure the necessary cooling; air (nitrogen and oxygén) and other diatomic gases require a somewhat greater expansion, and a polyatomic gas such as ethyl chloride requires so great an expansion that it is difficult to prevent leakage into the apparatus. In the latter case the leather gasket of the piston must also be lubricated with some material not soluble in ethyl chloride (as glycerol and graphite).

The writers wish to thank the Visual Education Society for the use of one of their motion picture cameras; the Gibb's Fund of the National Academy of Sciences for a grant partly used in this work; Dr. H. N. McCoy for the polonium used and for the loan of radium; Dr. H. S. Miner of the Welsbach Company, for the loan of mesothorium and radiothorium; Mr. Henry Burke, of Burke and James, Chicago, for aid in securing the remarkably fine lens used; and Mr. Paul L. Gross for assistance in the photographic work.

Summary

1. The rarity of a collision between a fast helium nucleus (α -particle) and the nucleus of an atom in a gas through which it is passing, increases

greatly as the directness of the collision increases. At the time of the beginning of the experimental work described in the present paper no photograph of a collision had been obtained sufficiently sharp to give the helium nucleus (α -particle) a retrograde motion after the collision. Thus far photographs have been taken of enough tracks so that the α -particles have passed through about 12 billion atoms in air, with the result that in only 3 cases has such a rebound been obtained. This alone would indicate that the nucleus of an atom of nitrogen or oxygen is of the order of slightly more than 10^{-13} cm. in radius. A more accurate value can be obtained by a mathematical analysis of all of the deflections of the α -particle through smaller angles.

- 2. In an ordinary collision 3 tracks meet in a point: one for the α particle before, and a second for the same particle after the collision. If the bombarded nitrogen or oxygen nucleus should disintegrate, then at least 4 tracks should meet, the additional track being due to a fragment, such as an electron, a hydrogen or a helium nucleus, disrupted from the bombarded nucleus. The chance of such a disintegration increases rapidly with the directness of the collision, and with the speed of the α -particle. For some unknown reasons the tracks of high-speed α -particles have not been photographed in previous work. While using such high-speed particles the writers secured a remarkable photograph of by far the most direct nuclear collision recorded in this way up to the present time, with the result that a fourth track, which should characterize an atomic disintegration, appeared in the photograph. That this track springs from the proper point in space is shown by the two projections obtained simultaneously. These give two views at an angle of 90°. Whatever may be the final decision with respect to this individual photograph, the method presented in this paper will reveal atomic disintegrations to give either helium or hydrogen or electrons, provided they occur during the operation of the apparatus, though the labor and expenditure of funds involved in obtaining such photographs may prove to be very great.
- 3. Rays of a new type, designated by the writers as zeta (ζ) rays, are shown in Fig. 6. Here the α -particle evidently drives particles from 2 widely separated atoms in its path. It is remarkable that the two tracks thus obtained lie in almost parallel planes, both are highly curved and almost parallel lines, and both have a sharp retrograde motion. It seems probable that the ζ -rays are due to electron emission, but this is not certain. The particles must be very light, however, since the direction of the α -particle is not materially affected by the emission, and the tracks of the particles are moderately long, very much longer than those of the previously recorded δ -rays.
- 4. Thus far, 40,000 photographs have been secured, and 3,000 photographs are obtained for each additional hour of operation of the apparatus

with photographic attachments. A number of collisions have been observed visually during periods when the camera is not in use.

5. The method presented in this paper is being used to test experimentally the stability of atom nuclei. Such tests have not been made before. Rutherford's experiments, for example, reveal the disintegration of an extremely minute number of atoms to give long range hydrogen particles, but they do not show whether or not α - or any other short range particles are emitted. The difficulty of the present method lies in the small number of direct hits obtained. Less direct impacts are relatively numerous.

The remarkable feature of the present work is that in no case has any one of these oblique impacts effected a disintegration of the nucleus. Even more remarkable is the fact that the argon nucleus in Fig. 7 remains intact even under the sharp impact of a helium nucleus from Thorium C' (α -particle) with a velocity of 25,000 or 30,000 times that of the swiftest rifle bullet, immediately before impact. This is evidenced by the fact that the visible tracks around the point of collision exhibit conservation of momentum. Fig. 1 illustrates the stability of an atom of air (nitrogen or oxygen) in exactly the same way except that the velocity of the α -particle just before impact is not quite so high.

It may be added that the photographs chosen for this paper have been selected altogether from the standpoint of the importance of the events they represent, even although they may not be so good as some of the others from the purely photographic viewpoint.

CHICAGO, ILLINOIS

[Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 152]

THE EQUATION OF STATE FOR PURE NITROGEN, GAS PHASE¹

By Leighton B. Smith and Robert S. Taylor Received June 25, 1923

Following the method of Keyes, pure nitrogen has been investigated by the isometric method. The theoretical work in connection with the equation of state^{2,3,4,5} has made it appear highly probable that in the

¹ This investigation was undertaken by the Research Laboratory of Physical Chemistry at the request of the Bureau of Mines, working in coöperation with the War and Navy Departments. The Bureau of Mines as well as the Massachusetts Institute of Technology contributed liberally in funds needed to carry forward the work.

The present paper is the fourth published by this Laboratory presenting data required in perfecting the processes for the extraction of helium from natural gas.

- ² Phillips, (a) J. Math. Phys., Mass. Inst. Techn., 1, 42 (1921); (b) Proc. Nat. Acad. Sci., 7, 172 (1921).
 - ³ Keyes, This Journal, 43, 1452 (1921).
 - ⁴ Keyes, J. Math. Phys., Mass. Inst. Techn., 1, 89 (1922).
 - ⁶ Keyes, Proc. Nat. Acad. Sci., 3, 323 (1917).

case of a fluid composed of molecules of invariable type, the pressure should vary linearly with the temperature at constant volume. The truth of this proposition involves the consequence that the potential energy of any given species of molecule or atom should be a function of the volume only. The derivative of the potential energy or the cohesive pressure, as it has come to be designated, may be directly evaluated for each constant volume setting employed in the isometric method. The form of function which represents the cohesive pressure as well as the volume correction term is known and indeed the constants of the equation of state may be easily evaluated directly from the isometric data.

The constants for the equation of state for atmospheric nitrogen based on the data of Amagat have been published by Keyes. Sufficient data, however, for pure nitrogen are not available and the purpose of the present work is to provide accurate data from which the fundamental constants for nitrogen may be deduced. Certain improvements in method and a greater accuracy in the volume control of the apparatus have been attained as a consequence of this study.

Preparation of Pure Nitrogen

The nitrogen was prepared by heating a mixture of ammonium sulfate and potassium nitrite in solution.

Fig. 1 illustrates the apparatus employed for generating and purifying the gas. The flask A was partially filled with a concentrated solution of ammonium sulfate and a solu-

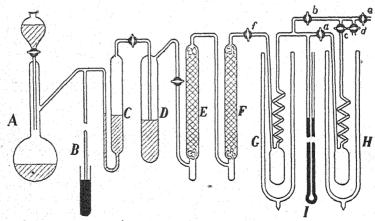


Fig. 1

tion of potassium nitrite was introduced from the separatory funnel, drop by drop. A safety tube and manometer B served to indicate the pressure and to relieve it, if it became excessive. The evolution of nitrogen was readily controlled by the heating and the rate at which the solution was admitted.

The gas first passed through concd sulfuric acid in the wash bottle C, then through a 20% solution of potassium hydroxide in D. E and F contained solid potassium hydroxide

droxide and phosphorus pentoxide, respectively. The gas was next passed through the bulb and spiral G immersed in liquid air which served to freeze and thus remove a large proportion of the impurities. From G the nitrogen passed to a similar arrangement at H which was immersed in liquid air through which hydrogen was bubbled. This so lowered the temperature of the liquid air that the nitrogen condensed to a liquid under a pressure of slightly more than 1 atmosphere. When a sufficient quantity of nitrogen had condensed in the bulb at H (about 20 cc.) the stopcocks a and f were closed and b and d opened, connecting G with the vacuum pump. G was now allowed to warm and the impurities that had condensed there were pumped away. The cock b was now closed and a opened for a short time, thus causing a portion of the liquid nitrogen to boil off and sweep out any fixed gaseous impurities in the vapor at H. The bulb and spiral at G were again cooled with liquid air through which hydrogen was then bubbled. The cock a was again opened and the bubbling of hydrogen at H stopped. As the temperature at H increased to that of liquid air boiling under 1 atmosphere pressure, the nitrogen slowly distilled from H and condensed at G. This process was stopped before all the liquid at H had disappeared and a was closed and C opened so that the residual nitrogen together with the impurities remaining in it were removed by the pump. This process of fractional distillation between G and H was repeated 5 times, and in each case the first and last fractions of distillate were discarded. The resulting liquid nitrogen was water-white and entirely free from particles of solid impurities. Finally, connection was made to the 6-liter Pyrex globe, which had previously been highly evacuated, and the nitrogen allowed to vaporize and fill the globe to somewhat over 1 atmosphere pressure.

The Pressure Gage

The gage was that employed by Keyes, Smith and Joubert⁶ in the work on the equation of state for methane gas phase and was of about 1 cm. in diameter.

It was calibrated against an open top mercury column about 9 meters high. A platinum needle in the short arm of the column for electrical contact with the surface of the mercury was used for detecting the equilibrium of the column. Temperature control of the column was obtained by enclosing it in a channel-shaped support closed on the front side by adjustable pieces of cardboard. The electrical system for detecting equilibrium of the gage consisted of a telephone with an audion bulb in circuit as indicated in Fig. 2. This device made possible the use of very feeble currents in the contact circuit, thus avoiding emulsification of the oil at the surface of the mercury and so insuring very sharp make and break. This emulsification of the mercury and oil is of very great importance in the compressibility measurements as it amounts to removing a small quantity of mercury from the piezometer portion of the system and thus changing its volume.

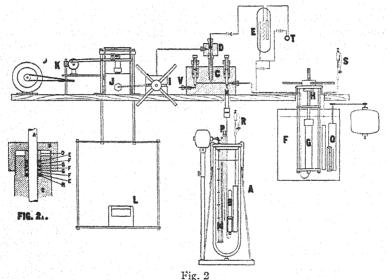
The length of the mercury column was measured on a steel tape, stretched by a load of 7 kg., which had been calibrated under the same stretching load by comparison with a standard meter compared at the United States Bureau of Standards. The complete data for the calibration of the gage have been published in the paper of Keyes, Smith and Joubert. The mean value of the constant is 1.0255 mm./g.

The Compressibility Apparatus and Method of Loading the Piezometer

The general apparatus is shown in Fig. 2, which is a further development of the apparatus used by Keyes and Felsing.⁷

- 6 Keyes, Smith and Joubert, J. Math. Phys., Mass. Inst. Techn., 1, 195 (1922).
- ⁷ Keyes and Felsing, This Journal, 41, 589 (1919).

The floating pressure piston with scale pan and motor for oscillating the piston is represented at J, L and K. The oil injector I serves to adjust the height of the floating piston and to compensate for leak of oil around the floating piston. The steel block C contains a stopcock V for exhausting and an insulated needle D for indicating the mercury level. This contact serves to detect equilibrium of the load on the piston and the pressure exerted by the material in the piezometer. For example, if too great a weight is on the piston the mercury will be depressed, and if too small a weight it will rise and make contact; 1 g. suffices, as a rule, to make or break the contact. A shut-off is provided for closing the piezometer B from the entire apparatus while connection is made from the block C to the mercury volume-displacement piston apparatus G submerged in a constant temperature bath F, whose contents are stirred by means of the motor and propeller apparatus Q. The nut H serves to force the piston into the mercury, driving it through fine steel tubing of small bore into the piezometer. The advance of the piston is indicated by 100 divisions engraved on the under portion of the nut. Whole turns are It is possible with the 16mm. piscounted by a "cyclometer" not shown in the drawing.



ton driven by a screw with 7.1 threads per cm. to estimate 0.001 turn of the nut, corresponding to about 0.00028 cc. The packing of the piston which moves into the cylinder G consists of cotton fabric heated in ceresin wax to 160°, and hard rubber forced into place by means of a steel ring driven by a screw cap.8 The packing is perfectly tight over long

⁸ The diagram, Fig. 2a, shows the method of applying the packing to the piston in the mercury volume injector. The piston is represented by A and the nut driving the packing at B through pressure on the steel ring D. At the bottom of the packing gland is a steel ring H which also is a snug fit to the piston. E, E indicate hard rubber rings and F,F,F the cotton fabric (such as unbleached cotton) impregnated quickly with ceresin wax at 160°. G,G are rings of soft steel. The annular width of the packing gland is about 3 mm. and the depth for moderate pressures (500 atm.) about 3 to 4 cm. The hard rubber ring protects the waxed packing from the kerosene of the bath and serves to wipe the piston as it moves backward and forward, thus minimizing the removal of wax. This latter objective is not as satisfactorily accomplished as desirable, but no better method of wiping the piston has been applied.

periods of use after having been seasoned by exposing it to several hundred atmospheres with successive tightenings of the driving nut. A similar packing is used on the stopcocks of the block C.

The constant temperature bath represented at A, Fig. 2, consists of a Pyrex Dewar tube 6.6 cm. in inside diameter and 40 cm. in length. The disposition of the platinum thermometer, stirrer, heater and mercury in the steel regulator is evident from the figure. For the bath fluid a high-boiling light oil sufficed for the range 50° to 200° , while an ice-bath served to maintain the piezometer at 0° . The cover of the bath is of asbestos wood and carries the bearing for the stirrer and binding posts for the electrical connections of the heater. The Dewar tube bath here represented is very convenient and has been employed to 330° . It possesses obvious advantages due to its permitting a view of the interior at all times, and the heat insulation is excellent. The Dewar tube, however, requires prolonged heating at 450° during exhaustion. Recent tubes silvered in such a manner as to leave a clear strip 2 cm. to 5 cm. in width parallel to the long axis have greater heat-insulating properties, at the same time permitting a view of the interior. The silver will not peel, once it has been slowly and thoroughly baked out during exhaustion.

The piezometer is represented in detail at A, Fig. 3. It was made in one piece from cold rolled steel, the lower end being spun shut and welded with the oxy-acetylene flame.

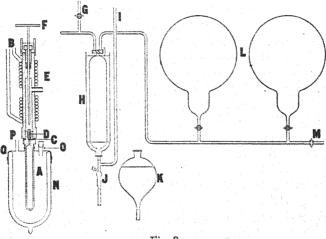


Fig. 3

A left-hand thread was cut on the outer portion, where it screwed into the top piece E surrounded by a cooling coil of copper B. The latter piece carried a screw driver F passing through a packing gland and sealed with mercury. The piezometer was locked by means of the plug D, which had a 0.75 mm. hole drilled throughout its length. The locking of the piezometer was secured by the compression of the gold washer C against a seat in the piezometer by means of the screw D. The purpose of the cooling coil about E was to preserve the packing gland during the exhaustion of the bomb at 350°.

Nitrogen is, of course, above its critical temperature at ordinary temperatures, and it was necessary to place in the piezometer sufficient nitrogen to give a range of volumes per gram from 5 to 23 cc. over the temperature range 0° to 200°. The capacity of the piezometer was 13.3143 cc. at 0° to the under surface of the gold disk. The quantity of nitrogen

employed was about $0.51~\rm g$., corresponding to about $410~\rm cc.$ at N.T.P. and producing about $40~\rm atmospheres$ pressure in the piezometer at ordinary temperatures.

The procedure of loading consisted in first exhausting the buret H connected by means of the 2-way stopcock with the piezometer, the latter being, of course, heated to drive off adsorbed matter. Nitrogen was then permitted to expand into H from the holders L and, when temperature equilibrium had been established, the pressure was read on the mercury column I. The buret was of the constant volume type, with the lower buret mark engraved on a tube of the same diameter as the manometric tube, thereby avoiding corrections for capillary depression. The nitrogen in the buret was transferred to the piezometer by cooling the latter in liquid air and raising the mercury reservoir K, thus liquefying the nitrogen in the piezometer. The vapor pressure of nitrogen at the temperature of liquid air is rather high, so the air was boiled under reduced pressure. For this purpose the Dewar tube containing the liquid air was provided with a spun cap of german silver Q that had an opening for the piezometer and tubes O and P for introducing liquid air and for connection with the vacuum pump. O could be closed with a rubber stopper. The cap was made fast to the Dewar tube and the piezometer by means of soft rubber tape and rubber cement. The air was boiled under a vacuum of 5 or 6 mm. of mercury which made it possible to liquefy the nitrogen under a pressure of 20 or 30 cm. The piezometer was then locked by screwing down the screw D by means of the screw driver F. The nitrogen remaining in the leads and in E above the gold disk was removed by means of a Toepler pump and the volume measured at a known temperature and pressure. To obtain the true mass requires the equation of state for nitrogen, or it suffices for the accuracy obtainable9 to employ the weight of a liter at N.T.P.

The weight of a liter of pure nitrogen was taken as 1.2507 g., or the volume of a gram is 799.55 cc. as given by Moles.¹⁰ Holborn and Otto¹¹ found for their nitrogen 1.2509 g., in fairly good agreement with the above. Later in this paper further reference to the matter of the weight of a liter of pure nitrogen will be made.

⁹ The gas is measured in the buret H, Fig. 3, under other conditions of temperature and pressure than N.T.P., under which the liter is measured. Strictly, one should know the compressibility and coefficient of expansion of the gas to obtain the true weight of the quantity actually measured. The use of the perfect-gas laws with the measured weight per liter leads to no appreciable error, however, in the case of nitrogen, as was proved when the constants of the equation of state were obtained. It will be shown in the present paper that the weight of a liter of nitrogen calculated by the equation of state agrees very well with the experimental determination of Moles.

¹⁰ Moles, J. chim. phys., 19, 283 (1922).

¹¹ Holborn and Otto, Z. Physik, 10, 367 (1922).

The loaded piezometer is connected with a piece of hexagonal steel carrying a steel tubing of 0.75 mm. bore locking against an annealed aluminum washer, and placed inverted in the constant-temperature bath. Referring again to Fig. 2, the piezometer with its steel tube may then be connected with the block C and the steel lead exhausted through V to the gold washer serving to confine the nitrogen in the piezometer. After closing the stopcock in block C at V, mercury may be run in by screwing in the piston of the mercury volume-injector G. It is to be added that a plug replaced the oil lead from I in D during the exhaustion and the oil lead was replaced after filling the block and lead with mercury. The oil lead having been connected, mercury is brought to the needle point by manipulating the oil injector I and volume injector G. By this means a zero setting may be obtained at a definite pressure corresponding to the position of the mercury which is in contact with the gold disk closing the piezometer. After the zero setting is obtained the pressure is increased to several hundred atmospheres and in about 24 hours the gold disk, weakened by amalgamation with the mercury, is punctured, bringing the mercury into contact with the nitrogen. By means of the mercury injector G a setting may be made for a chosen specific volume of nitrogen and a series of pressures and temperatures observed.

It is necessary to know expansion of the mercury with the temperature as well as its compressibility¹² while the stretch of the steel piezometer and apparatus may be obtained by separate blank measurements. For the true expansivity with temperature of the steel piezometer, the data of the Reichsanstalt were correlated as a function of the temperature as follows.

$$V_t^{Fe} = V_0 (1 + 3.25 \times 10^{-5} t + 2.85 \times 10^{-8} t^2 - 1.65 \times 10^{-11} t^3)$$

The equation for the volume of mercury as a function of the temperature, as given by Callendar and Moss, was employed.

$$V_t^{Hg} = V_0 (1 + 1.80555 \times 10^{-4} t + 1.2444 \times 10^{-8} t^2 + 2.539 \times 10^{-11} t^3)$$

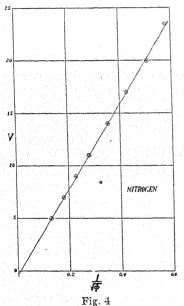
The shifting of the temperature requires, for preserving constancy of the nitrogen volume, a resetting of the mercury injector G to compensate

The compressibility of mercury is a function of both pressure and temperature. Thus Bridgman gives the compressibility at 1 atmosphere as 3.80×10^{-6} at 0° and 3.95×10^{-6} at 22° . The decrease of the compressibility with pressure is given as about 3% for the first thousand atmospheres. The effect of increase in pressure may be neglected in the present work since 400 atmospheres was not exceeded. The temperature effect on the stretch of the piezometer is determined as the sum of that due to the compressibility of the mercury contained in the piezometer and the stretch of the piezometer itself. These direct measurements failed to disclose any pronounced effect on the combined mercury compressibility and piezometer stretch because of the small amount of mercury (13.3 cc.) contained in the piezometer and the smallness of the temperature coefficient of stretch of the piezometer. The value 3.9×10^{-6} was assumed for the mercury compressibility independent of the temperature. The total stretch of the piezometer amounted to 9.73×10^{-6} cc. per atm.

for the combined increase in volume of the mercury in the piezometer and the dilation of the piezometer with temperature and pressure. The method of making this computation is obvious, when the stretch of the piezometer and apparatus with pressure and the expansion of the piezometer and mercury with temperature are known.

The Experimental Data

The data were taken first at 50°, continued to 100°, 150° and 200°, and the observations at 0° were made last, using a Dewar tube filled



with ice. In Table I will be found the absolute temperatures and pressures for the fixed volumes beginning with 23 cc. per g. of nitrogen. A linear equation is given with each volume which has been used to calculate the pressures recorded under each observed pressure.

The equation of state gives, for the tangent of the pressure-temperature lines at constant volume, the expression $R/(v-\delta)$. The magnitude of R per mole is known with tolerable accuracy, ¹³ being 82.058 cc., atm. per degree C., per mole. The molecular weight of nitrogen has been taken as 28.02. The value of R per g. of nitrogen is, therefore, 2.92855.

From the equations for the isometrics the constants for the cohesive pressure term $\Phi = A/(v-l)^2$ may be derived. The constant of the linear equation for each

volume is equal to Φ for that volume. These values were calculated over to $1/\sqrt{\Phi}$ and plotted against v giving a straight line as shown in Fig. 4.

When we represent this by an equation of the form $V = a + \frac{b}{\sqrt{\Phi}}$, we see

Table I
Observed Pressure Represented as a Linear Function of the Temperature at
Constant Volume

Volume Cc.	0°	49.98° p = 1	100° 0.136096 <i>T</i> —	152.34° 2.9794	200°	Pressure
23	34.175	41.012	47.812	54.930	61.380	Obs.
	34.193	40.896	47.804	54.927	61.413	Calc.
		<i>p</i> =	0.157963T-	-3.8947		
20	39.251	47.141	55.088	63.322	70.839	Obs.
	39.251	47.146	55.048	63.315	70.844	Calc.

¹³ Keyes, J. Am. Soc. Refrig. Eng., 8, 505 (1922).

that l=-a and $A=b^2$. In Table II are listed the observed Φ 's and those calculated from the equation $\Phi=\frac{1623.6}{(v+0.2954)^2}$.

TABLE II

COHESIVE PRESSURE DEDUCED FROM INTERCEPTS OF STRAIGHT-LINE EQUATIONS COMPARED WITH COHESIVE PRESSURE CALCULATED BY MEANS OF THE EQUATIONS

			5732
$\Phi = \frac{16}{(v+1)^2}$	323.6 0.2954) ² (Eq. a), an	$d \Phi = \frac{1623.3}{v^2} e$	v (Eq. b)
Volume Cc.	Φ	Φ Calc. from Eq. a	Φ Calc. from Eq. b
23	2.979	2.992	2.993
20	3.895	3.942	3.944
17	5.523	5.428	5.431
14	8.019	7.945	7.950
11	12.733	12.726	12.735
9	19.373	18.791	18.804
7	30.478	30.506	30.524
5	57.900	57.901	57.900

To complete the equation of state it remains to obtain the constants for the δ equation. δ was calculated for each observed pressure from the relation $\delta = v - \frac{RT}{p+\Phi}$. The values for each volume were averaged and the mean values log δ were plotted against 1/v. The plot is reproduced in Fig. 5, showing that nitrogen follows the function $\delta = \beta e^{-\alpha/v}$.

The complete equation of state for nitrogen is, therefore,

$$\dot{p} = \frac{2.92855}{v - \delta} T - \frac{1623.6}{(v + 0.2945)^2}, \ \log_{10} \delta = 0.18683 - \frac{0.3113}{v} \tag{1}$$

TABLE III VALUES OF & FOR INDIVIDUAL TEMPERATURES CALCULATED FROM OBSERVED PRESSURES 1623.63

AND THE VALUE OF Φ GIVEN BY THE EQUATION Φ $(v + 0.2954)^2$ Volume Cc. 00 49.98° δ Mean 100° 152.34° 200° & Calc. 1.4854 1.490 1.4749 1.4958 1.4908 1.487623 1.47811.4754 1.4711 1.4782 1.483 1.4758 1.4881 20 1,4807 1.4624 1.4698 1.4886 1.4705 1.46521.47531.474 17 1.4610 1.461 14 1.4584 1.45241.47211.46291.45941.4324 1.44281,441 11 1.4438 1.44321.4499 1.4446 1.4279 1.4160 1.4234 1.420 9 1.4178 1.42501.4301 7 1.3854 1.3931 1.3934 1.3902 1.3824 1.3888 1.388 1.3328 1.3320 1.3324 1.3336 1.32891.3319 1.332 5

In Table IV will be found the pressures calculated by means of Equation 1 for comparison with the observed values.

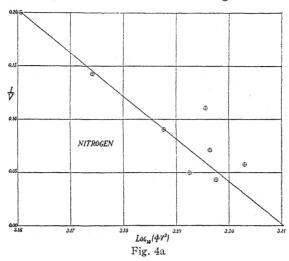
	TABLE 1V		
	Nitrogen	ISOMETRICS	
0.0°	49.98°	100.00°	
273 14 9	323 120	272 14°	

			NITROGEN	ISOMETRICS			
Sp. vol.	27 P).0° 3.14° ress. atm.	49.98° 323.12° Press. atm.	100.00° 373.14° Press. atm.	152.34° 425.48° Press. atm.	200.00° 473.14° Press. atm.	
23	Obs.	34.175	41.012	47.812	54.930	61.380	
20	Calc.	34.196	41.000	47.810	54.936	61.425	
20	Obs.	39.251	47.141	55.088	63.322	70.839	
	Calc.	39.256	47.198	55.072	63.350	70.887	
17	Obs.	46.054	55.503	65.021	74.809	83.766	
	Calc.	46.092	55.520	64.955	74.827	83.817	
14	Obs.	55.835	67.470	79.281	91.443	102.545	
	Calc.	55.848	67.521	79.204	91,428	102.559	
11	Obs.	70,979	86.290	101.698	117.676	-132.197	
	Calc.	70.955	86.267	101.591	117.626	132.228	
9	Obs.	86.707	106.130	125.564	145.765	163.911	
	Calc.	86.737	106.047	125.372	145.594	164.008	
7	Obs.	111.962	138.263	164.401	191.614	216.152	
	Calc.	112.029	138.110	164.212	191.525	216.396	
5	Obs.	160.224	200.153	240.052	281.956	319.534	
	Calc.	160.175	200.080	240.016	281.804	319.856	
	$p = \frac{RT}{v - \delta} - \frac{1623.63}{(v + 0.2954)^2}$ where $\log \delta = 0.18683 - \frac{0.3113}{v}$						
	$v = \overline{v}$	$-\delta - \overline{(v)}$	$+0.2954)^{2}$ W1	iere log 0 = i	0.10000	v	
R = 2.92855					76 and $\alpha =$	0.7169	

$$p = \frac{RT}{v - \delta} - \frac{1623.63}{(v + 0.2954)^2} \text{ where log } \delta = 0.18683 - \frac{0.3113}{v}$$

$$R = 2.92855 \qquad \beta = 1.5376 \text{ and } \alpha = 0.716$$

It seems probable that the true form of the cohesive-pressure equation is $\frac{A'}{m^2}e^{-l'/v}$ where A' and l' are constants of similar significance to the constants in the form $A/(v+l)^2$. In the gas phase it is difficult to distinguish between the two forms. Thus $\frac{A'}{n^2}e^{-\nu/\eta}$ for large volumes becomes, with sufficient accuracy, equal to $\frac{A'}{v^2}\left(1-\frac{l'}{v}\right)=\frac{A'}{v^2\left(1+\frac{l'}{2v}\right)^2}\equiv\frac{A}{(v+l)^2}$. Hence, for the gas phase A = A' and 2l = l'. In order to determine the constants of this exponential form, one takes logarithms of both sides,



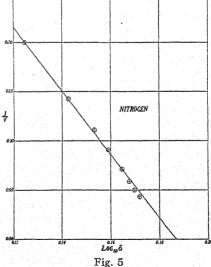
whence one gets $\log \Phi = \log \frac{A}{v^2} - \frac{l'}{v}$. Hence, a plot of $\log \Phi v^2$ against

1/v should give a straight line. Fig. 4a shows that a straight line is all that the assemblage of points will justify. Giving most weight to the

high-pressure points, since they always serve to locate the constants better than low-pressure data, one obtains the following constants: A = 0.286. This is an excellent check and shows that the two forms are interchangeable as far as the present data go. The equation is $\log \Phi = \log \frac{1623.3}{v^2} - \frac{1623.9}{v^2}$. In Table II are also given

the values of Φ calculated from this second form.

Weight of a Liter of Nitrogen at Normal Temperature and Pressure



Moles has most recently measured the normal density of nitrogen¹⁰ obtaining 1.2506 g. per liter as the mean of four volumetric determinations in good agreement with the mean value 1.2507 of 29 determinations by four authors using two different experimental methods with nitrogen produced by eight different reactions. Holborn and Otto¹¹ as a test of the purity of their nitrogen determined the weight of a liter to be 1.2509 g. The equation of state gives 779.40 cc. as the volume of 1 g. at 0° and 1 atm. pressure. The reciprocal of this multiplied by 1000 gives 1.2509 as the weight of 1 liter at N.T.P.

Equation of State for Atmospheric Nitrogen from Measurements by Amagat

Amagat¹⁴ has measured the isotherms for gaseous atmospheric nitrogen. The data are divided into two series, the first set extending over a range of pressure from 100 to 1000 atmospheres and from 0.0° to 199.5°. The second series covers the range of pressures from 1000 to 3000 atmospheres and from 0.0° to 43.6°. The volumes given are relative to the capacity of a manometric tube and are not absolute. Keyes¹⁵ has derived an equation from the low-pressure measurements which he gives as

$$\dot{p} = \frac{2.9138}{v - \delta} T - \frac{1587.2}{(v - 0.007)^2}, \quad \log \delta = 0.2200 - \frac{0.284}{v}$$

He assumes the composition of atmospheric nitrogen to be 1.66% argon and 98.34% nitrogen by weight. The apparent molecular weight is taken as 28.163. The volume of 1 g. is taken as 795.12 cc.

Rayleigh, ¹⁶ Regnault, Von Jolly and Leduc have determined the weight of a liter of atmospheric nitrogen. Regnault's value was corrected by Crafts for contraction of the globe and Von Jolly's was corrected by Rayleigh. Rayleigh's and Leduc's values are the latest available and are in best agreement. The mean of their values, 1.25714 g., was assumed as the best figure for the weight of a liter. This gives 795.46 cc. as the volume of 1 g.

Two methods are available for determining the apparent molecular weight. From the weight of a liter of argon, 1.78094, 17 the weight of a liter of pure nitrogen 1.2507 and the weight of a liter of atmospheric nitrogen, the composition of atmospheric nitrogen may be calculated. This method, which is not very accurate, gives 1.21% of argon.

Guye¹⁸ gives the percentage by volume of oxygen in air as 20.94 and the weight of 1 liter of air as 1.2928 g. Keyes¹³ gives 699.77 cc. as the best value for the volume of 1 g. of oxygen. Therefore, we obtain 23.147% oxygen by weight. Moureu and Lepape¹⁹ give the percentage of argon in air as 1.29 by weight. From this, the composition of atmospheric

¹⁴ Amagat, Ann. chim. phys., 29, 68 (1893).

¹⁸ Keyes, This Journal, 42, 54 (1920).

¹⁶ Rayleigh, "Scientific Papers," Vol. IV, 51 (1893), or Proc. Roy. Soc., 53, 134 (1893).

Watson, J. Chem. Soc., 97, 833 (1910).
 Guye, J. chim. phys., [4] 15, 570 (1917).

¹⁹ Moureu and Lepape, Ann. chim., [9] 4, 5, 4 (1915).

nitrogen is 1.679% argon and 98.321% nitrogen by weight. This gives for the apparent molecular weight $\frac{1}{\frac{0.01679}{39.88} + \frac{0.98321}{28.020}} = 28.161 \text{ using the}$

accepted values of 39.88 and 28.020 for the molecular weights of argon and pure nitrogen. The gas constant R per gram is, therefore, 82.058/28.161 = 2.9139, which coincides with that obtained by Keyes.

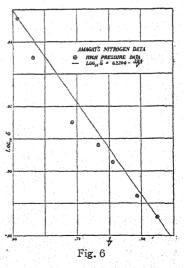
TABLE V
AMAGAT'S HIGH PRESSURE ISOMETRICS

Vol. actual cc./g.	Vol. A units	0° Press. atm.	16.0° Press. atm.	43.6° Press. atm.	16.0° Press. calc, from st. line eqs.	Eq.
1.647	0.00207	1000	1088	1239	1087.7	1
1.548	.001946	1200	1298	1474	1300.6	2
1.443	.0018135	1500	1613	1812	1614.5	3
1.364	.0017145	1800	1937	2168	1935.0	4
1.323	.0016635	2000	2150	2401	2147.2	5
1.260	.0015835	2400	2572	2858	2568.1	6
1.213	.0015250	2800	2990			7
1. $p = 5$	$.482\ T\ -\ 497.36$	3	5. p	= 9.197	r - 512.1	
2. $p = 6$	$.284\ T-516.4$		6. p	= 10.505 2	r - 469.3	
3. $p = 7$	$.156\ T\ -\ 454.6$		7. p	= 11.875 2	r - 443.5	
4. $p = 8$.440 T - 505.3					

Amagat's series for 1000 to 3000 atmospheres extends over a very short temperature range. Table V gives his constant volume values

and also the actual volumes in cc. per g. as obtained by multiplying his relative volumes by 795.5. Straight-line equations were passed through the points at 0.0° and 43.6° and are given below Table V. In Col. 6, Table V are given the pressures at 16.0° calculated from the corresponding constant-volume equations. These show that, within Amagat's limits of accuracy, p is a linear function of T at constant volume up to 3000 atmospheres.

In Fig. 6 the line represents the plot of $\log \delta$, as calculated from Keyes' equation, against 1/v. The points represent the observed values obtained from Amagat's high-pressure series. The fact that all of the observed points fall upon one side of the



line indicates that Amagat's low-pressure series is not entirely concordant with his high-pressure series.

Comparison of the Recent Work of Holborn and Otto with the Equation of State for Nitrogen

Holborn and Otto¹¹ have recently measured the products of $p \times v$ for oxygen, nitrogen and helium. They represent their data by equations of the form pv = f(p) and pv = f1/v. For the second form they give equations representing the 0°, 50° and 100° isotherms for nitrogen, which when converted to v in cc. per g. and p in atmospheres are as follows:

$$pv = (pv)_0 \left(1 - \frac{0.4563032}{v} + \frac{2.92858}{v^2}\right) \text{ at } 0.0^{\circ}$$
 (2)

$$pv = (pv)_0 \left(1 - \frac{0.0262332}{v} + \frac{3.06343}{v^2}\right) \text{ at } 50.0^{\circ}$$
 (3)

$$pv = (pv)_0 \left(1 + \frac{0.279970}{v} + \frac{3.18418}{v^2}\right) \text{ at } 100.0^{\circ}$$
 (4)

From the equation of state,

$$pv = RT \frac{v}{v - \delta} - A \frac{v}{(v + l)^2}$$

Expanding this in the form of a series gives

$$pv = RT \, v \left(\frac{1}{v} + \frac{\delta}{v^2} + \frac{\delta^2}{v^3} + \frac{\delta^3}{v^4} + \dots \right) - Av \left(\frac{1}{v^2} - \frac{2l}{v^3} + \frac{3l^2}{v^4} + \dots \right)$$

but

$$\delta = \beta e^{-\alpha/v} = \beta \left(1 - \frac{\alpha}{v} + \frac{\alpha^2}{2v^2} - \frac{\alpha^3}{6v^3} + \dots \right)$$

Neglecting all terms of higher order than $1/v^2$ there is obtained

$$pv = RT \left[1 + \frac{1}{v} \left(\beta - \frac{A}{RT} \right) + \frac{1}{v^2} \left(\beta^2 - \alpha \beta + \frac{2Al}{RT} \right) \right] \tag{5}$$

Since $(pv)_0 = RT$, Equation 5 is seen to be, at constant temperature, of the same form as Equations 2, 3 and 4. Substituting in (5) the constants of the equation of state for 0.0° , 50.0° and 100.0° one obtains the following equations for comparison with those of Holborn and Otto.

$$pv = (pv)_0 \left(1 - \frac{0.49227}{v} + \frac{2.45735}{v^2} \right) \text{ at } 0.0^{\circ}$$

$$(pv)_0 = RT = 799.890$$
(6)

$$pv = (pv)_0 \left(1 - \frac{0.17819}{v} + \frac{2.27236}{v^2} \right) \text{ at } 50.0^{\circ}$$

$$(pv)_0 = 946.317$$
(7)

$$pv = (pv)_0 \left(1 + \frac{0.05172}{v} + \frac{2.13694}{v^2} \right) \text{ at } 100.0^{\circ}$$

$$(pv)_0 = RT = 1092.745$$
(8)

For comparison purposes there are given in Table VI, values of pressures in atmospheres and corresponding volumes in cc. per g. at 0° , 50° and 100° from determinations by Holborn and Otto. These values for volume were converted from the arbitrary units by multiplying the latter by the factor 607.43 which is that given by the equation of state when p = 1 meter p = 1.31579 atm. and p = 1 meter p = 1.31579 atm. and p = 1 meter p = 1.31579 atm. and p = 1 meter p = 1.31579 atm.

Table VI
PRESSURES AND VOLUMES COMPUTED FROM EQUATIONS BY HOLBORN AND OTTO

Press. meters of Hg	Press. atm.	0°	Volumes (cc. per g. 50°	100°
10	13.158	60.449	71.930	83.266
30	39.474	19.993	24.022	27.951
50	65.789	11.943	14.477	16.920
70	92.105	8.532	10.418	12.214

From the equation of state pressures were calculated corresponding to the volumes given in Table VI.

These values are listed in Table VII.

TABLE VII

Pressures from Equation of State using Volumes and Temperatures from

			LABL	E AT			
	0.0		5	0,0	100	100°	
7'		t	21	Þ	? *	Þ	
60.449		13.134	71.930	13.128	83.266	13.135	
19.993		39.270	24.022	39.257	27.951	39.275	
11.943		65.376	14.477	65.275	16.920	65.268	
8.532		91.533	10.418	91.203	12.214	91.142	

The pressures resulting from the present work corresponding to the volumes and temperatures given by Holborn and Otto are seen to be lower at about 90 atm. by 0.6%. It will be pointed out subsequently that until the "pure" nitrogen chemically prepared had been fractionated to remove traces of nitric oxide the higher pressures were obtained.

In Table VII of Holborn and Otto's paper are given values of the pv product at 0° , 50° and 100° for various constant densities. The values of 5, 15, 25, 35, 45 and 55 in their arbitrary units were chosen. Multiplying the pv products by the density gives the pressures in meters. Converting the densities to cc. per g. and the pressures to atmospheres, as explained above, the values contained in Table VIII were obtained.

TABLE VIII
PRESSURES AT CONSTANT VOLUME FROM HOLBORN AND OTTO

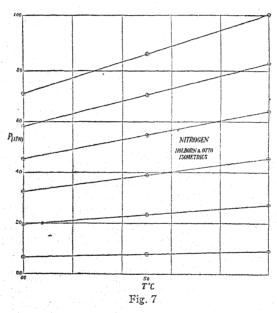
<u>1</u>				
v (arb. units)	(cc. per g.)	0°	—Pressures (atm.)—— 50°	100°
5	121.486	6.564	7.789	9.010
15	40.495	19.596	23.383	27.149
25	24.297	32.535	39.025	45.493
35	17.355	45.416	54.760	64.096
45	13.498	58.261	70.639	83.021
55	11.044	71.105	86.727	102.303

The above values of pressure are plotted against the absolute temperature as shown in Fig. 7. These constant volume lines are straight to within what is believed to be the accuracy of Holborn and Otto's results.

From Equation 5 we see that the coefficient of 1/v in the pv product

equation is equal to $\beta - \frac{A}{RT}$. Taking the coefficients of 1/v in Equations 2, 3 and 4 of Holborn and Otto and solving simultaneously for A we obtain the 3 values 2223.2, 2162.4 and 2197.5, of which the mean is 2194.4. Substituting this mean value of A we obtain for β the 3 values 2.287, 2.293 and 2.288, of which the mean is 2.289.

Holborn and Otto prepared nitrogen from sodium nitrite and purified it by passing it through alkaline pyrogallol and over glowing copper. It is known that alkaline pyrogallol is likely to introduce carbon monoxide and Smyth and Roberts²⁰ have shown that unless the temperature of the copper is kept below 600° the copper oxide will decompose and introduce



oxygen. Also, copper will not reduce oxides of nitrogen unless the temperature is fairly high. The good agreement between the weight of a liter as determined by Holborn and Otto and the accepted value does not necessarily indicate great purity of the gas since, in the first place, the weight of a liter is very difficult to obtain and second, since the molecular weight of carbon monoxide is essentially the same as that of nitrogen and since nitric oxide has only a slightly greater molecular weight, the pressure of appreciable quantities of these gases would not greatly affect the weight of a liter, but would affect the magnitude of the A and β constants greatly. Previous to the work on the equation of state of pure nitrogen as given in this paper an equation was determined for a sample of gas purified by the

²⁰ Smyth and Roberts, This Journal, 42, 2582 (1920).

usual chemical methods. An A constant of about 1860 was obtained, which lies much nearer the value obtained above from Holborn and Otto's work. Subsequently it was found that when this sample of nitrogen was condensed, suspended solid impurities were observed in the liquid. After 5 fractional distillations a perfectly water-white liquid was obtained that was undoubtedly pure. This procedure was used in preparing the gas for the measurements upon which the equation of state was based. Since the impurities mentioned as likely to be present in nitrogen, purified by chemical means, are all less perfect gases than nitrogen, their presence in small amounts would tend to increase the magnitude of the constants.

Compressibility Coefficients

Maverick, 21 both alone and in collaboration with Batuecas, has made measurements on the compressibility coefficients at 1 atmosphere and 0°. Those made by Maverick alone seem to be more consistent than the $\frac{1}{2} \left(\frac{1}{2} \left(\frac{1}{2} \right) \right)$

others. His
$$\lambda$$
 is defined as equal to $-\frac{1}{(pv)_{760}} \left(\frac{\partial (pv)}{\partial p}\right)_T$.

His average value and those of other observers at 0° are Maverick, 0.00044; Chappuis, 22 0.00043; Leduc and Sacerdote, 23 0.00038; Rayleigh, 24 0.00056. Maverick's values for nitrogen prepared from urea were discarded because of impurities in the gas so prepared.

From Equations 2, 3 and 4 of Holborn and Otto values of λ are obtained as follows: 0°, 0.000561; 50°, 0.000023; 100°, —0.000360.

From Equations 6, 7 and 8 derived by the equation of state the following are obtained: 0°, 0.000608; 50°, 0.000216; 100°, —0.000071.

Owing to the extreme accuracy with which an observer must work in order to obtain any percentage accuracy for this coefficient, the agreement is about as good as can be expected. Keyes⁴ has worked over the values for compressibility coefficients of Chappuis, Leduc and Sacerdote, and Rayleigh, comparing them with values obtained from the equation of state for atmospheric nitrogen.

In conclusion it is desired to thank Professor F. G. Keyes for his valuable suggestions and assistance, without which this work could not have been carried out.

Summary

- 1. The p, v, T relationship of pure gaseous nitrogen has been studied by the isometric method over the range of temperatures from 0° to 200° and 30 to 330 atmospheres' pressure. The Keyes equation represented
- ²¹ Maverick, Thesis, University of Geneva, No. 708, Jan., 1923 (to be published soon in J. chim. phys. and Chim. Helvetica Acta).
 - ²² Chappuis, Trav. mem. bur. intern., 13, 66 (1903).
- ²³ Leduc, Ann. chim. phys., [7] 15 (1899); Compt. rend., 123, 743 (1896); 125, 297 (1897); 148, 407 (1909).
 - ²⁴ Rayleigh, Proc. Roy. Soc., 73, 153 (1904); Z. physik. Chem., 37, 713 (1901).

the data within the experimental limits of error. This equation obtained is, $p_{\text{atm.}} = \frac{2.92855\ T}{v-\delta} - \frac{1623.63}{(v+0.2954)^2}$ where log $\delta = 0.18683 - \frac{0.3113}{v}$.

- 2. The weight of a liter of nitrogen at N.T.P. was calculated from the equation of state to be 1.2509 g. as compared with the generally accepted value of 1.2507 g.
- 3. The compressibility coefficient at 0° was calculated and found to be 0.00061 as compared with 0.00056 from Holborn and Otto's equation and the work of Rayleigh, and 0.00043 and 0.00044 from Chappuis and Maverick, respectively.

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[Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 154]

THE MELTING POINT OF ICE ON THE ABSOLUTE TEMPERATURE SCALE

BY LEIGHTON B. SMITH AND ROBERT S. TAYLOR

Received June 25, 1923

Chappuis,¹ Day and Clement,² Holborn and Henning³ and Eumorfopoulos⁴ have made measurements on the expansion coefficients from 0° to 100° both for the constant volume and the constant pressure thermometers. Keyes⁵ calculated ϵ , the expansion coefficient for a perfect gas, using the data of the above-mentioned workers and the equation of state which he based on Amagat's data for atmospheric nitrogen. Since then Henning,⁶ and Henning and Heuse⁵ have done some work on expansion coefficients for nitrogen and some other gases. It is, therefore, thought worth while to review the above data using the new equation of state of nitrogen⁵ and also the method of obtaining ϵ using the equation of state, since this has never been given in detail before.

Instead of using a constant-pressure thermometer, a constant- π thermometer will be considered where π is defined by the equation $\pi\omega=RT$. From the Keyes equation of state $\omega=v-\delta$ or, for low pressures $\omega=v-\beta$ and $\pi=p+A/(v+l)^2$, which reduces at low pressures to the form, $\pi=p+(A/v^2)$.

- ¹ Chappuis, Trav. mem. bur. intern., 6, 59 (1888) and 13, 66 (1903).
- ² Day and Clement, Am. J. Sci., 26, 405 (1908).
- 3 Holborn and Henning, Ann. Physik, 35, 761 (1911).
- Eumorfopoulos, Proc. Roy. Soc. London, 90A, 189-203 (1914).
- ⁵ Keyes, This Journal, **42**, 54 (1920).
- ⁶ Henning, Z. Physik, 5, 264 (1921).
 - ⁷ Henning and Heuse, ibid., 5, 285 (1921).
 - ⁸ Smith and Taylor, This Journal, 45, 2115 (1923).

Then ϵ , the coefficient of expansion for a perfect gas, is given by the equation,

$$\epsilon = \left(\frac{\omega_t - \omega_0}{\omega_0 t_{(ab)}}\right)_{\pi} \tag{1}$$

where $t_{(ab)} = T - T_0$ or, in other words, is centigrade thermodynamic temperature. The above equation is, therefore, identical with the following,

$$\epsilon = \frac{v_t \pi - v_0}{(v_0 - \beta) \ t_{(ab)}} \tag{2}$$

where v_0 is the volume measured at 0° and v_t^{π} is the volume at t° when π has the same value as at 0° .

 $\epsilon_{p_0}^t$ is defined by the following equation,

$$\epsilon_{p_0}^{\ t} = \frac{v_t^p - v_0}{v_0 t_c} \tag{3}$$

where v_i^p is measured on the constant-pressure thermometer. The constant- π thermometer has never been investigated experimentally hence v_i^π must be eliminated from Equation 2. By adding and subtracting v_i^p from the numerator of Equation 2 the following is obtained.

$$\epsilon = \frac{(v_t^{p_0} - v_0) + (v_t^{\pi} - v_t^{p})}{(v_0 - \beta) \ t_{(ab)}}$$
(4)

Dividing numerator and denominator by v_0t_c , Equation 4 becomes

$$\epsilon = \left[\frac{v_t^{p_0} - v_0}{v_0 t_c} + \frac{v_t^{\pi} - v_t^{p_0}}{v_0 t_c} \right]_{\pi}$$
 (5)

Substituting from Equation 5

$$\epsilon = \left[\frac{\epsilon_p + \frac{v_t \pi - v_t p_0}{v_0 t_c}}{\left(1 - \frac{\beta}{v_0}\right) \frac{t_{ab}}{t_c}} \right]_{\pi} \tag{6}$$

Since p_t^{π} is very close to p_0 , Boyle's law may be assumed to hold without, in this instance, introducing too great an error, or $v_t^{\pi} p_t^{\pi} = v_t^{p_0} p_0$.

Hence $v_t^{\pi} = v_t^{p_0} \frac{p_0}{p_t^{\pi}}$. Using this relation, Equation 6 becomes

$$\epsilon = \frac{\epsilon_p + \frac{v_t p_0}{v_0 t_c} \left[\frac{p_0}{p_t \pi} - 1 \right]}{\left[1 - \frac{\beta}{v_0} \right] \frac{t_{ab}}{t_c}} \tag{7}$$

Since $\frac{v_t^{p_0}}{v_0} = \left(1 + \frac{\epsilon_p}{0^0}\right)$ and since the pressures are involved only in the correction term, Equation 7 may be written

$$\epsilon = \frac{\epsilon_{\rm p} + \frac{1 + \epsilon_{\rm p}^{t}}{t_{\rm c}} \left[\frac{p_{\rm 0} - p_{\rm i}^{\tau}}{p_{\rm t}^{\tau} \equiv p_{\rm 0}} \right]}{\left[1 - \frac{\beta}{v_{\rm 0}} \frac{t_{\rm ab}}{t_{\rm c}} \right]} \tag{8}$$

Furthermore,
$$\pi_{t} = \pi_{0}$$
; therefore $p_{t} + \frac{A}{(v_{t})^{2}} = p_{0} + \frac{A}{(v_{0})^{2}}$ or $p_{t} - p_{0} = \frac{A}{v_{0}^{2}} - \frac{A}{v_{t}^{2}}$. But $v_{t} = v_{0}(1 + \epsilon_{p}t_{c})$; therefore $p_{t} - p_{0} = \frac{A}{v_{0}^{2}} \left[1 - \frac{1}{(1 + \epsilon_{p}t_{c})^{2}} \right]$.

Therefore, $\frac{p_{0} - p_{t}}{p_{0}} = -\frac{A}{p_{0}v_{0}^{2}} \left[\frac{(1 + \epsilon_{p}t_{c})^{2} - 1}{(1 + \epsilon_{p}t_{c})^{2}} \right] = -\frac{A\epsilon_{p}t_{c}}{p_{0}v_{0}^{2}} \left[\frac{2 + \epsilon_{p}t_{c}}{(1 + \epsilon_{p}t_{c})^{2}} \right]$.

Equation 8 now becomes,

$$\epsilon \left(1 - \frac{\beta}{v_0}\right) \frac{t_{ab}}{t_c} = \epsilon_p - \frac{A \epsilon_p}{p e v_0^2} \left[\frac{2 + \epsilon_p t_c}{1 + \epsilon_p t_c} \right] \tag{9}$$

Since $t_c = 100 - t_{ab}$ and since $p_0v_0 = RT_0$, Equation 9 becomes

$$\epsilon = \epsilon_p + \frac{\beta \epsilon}{v_0} - \frac{A \epsilon_p}{R^2 T_0^2} \left[\frac{2 + \epsilon_p t_c}{1 + \epsilon_p t_c} \right] p_0 \tag{10}$$

or since in the correction term it suffices to say that $\epsilon_b = \epsilon = 1/T_0$,

$$\epsilon_p = \epsilon + \left[\frac{A}{R^2 T_0^3} \left(\frac{2 + \epsilon_p t_c}{1 + \epsilon_n t_c} \right) - \frac{\beta}{R T_0^2} \right] p_0 \tag{11}$$

It is now seen that with the aid of certain approximations which, however, are permissible since they involve only the correction factor, the limitation of the constant- π thermometer has been removed and the resulting formula is general.

In the case of the constant-volume coefficient the same procedure is employed but the derivation is very much simplified, as will be seen. For the constant- ω thermometer

$$\epsilon = \left[\frac{\pi_t - \pi_0}{\pi_0 t_{ab}}\right]_{\omega} = \left[\frac{p_t - p_0}{\left(p_0 + \frac{A}{v_0^2}\right)t}\right]_{\omega},$$

since constant ω is identical with constant volume and A/v^2 is independent of the temperature. By definition,

$$\epsilon_{\rm e} = \frac{p_{\rm e} - p_{\rm o}}{p_{\rm o} \ell}$$
. Hence, $\epsilon_{\rm o} = \epsilon + \frac{A \epsilon}{v_{\rm o}^2 p_{\rm o}}$, or $\epsilon_{\rm v} = \epsilon + \frac{A}{R^2 T_{\rm o}^3} p_{\rm o}$. (12)

From the equation of state of nitrogen, Equation 12 becomes $\epsilon_p = \epsilon + 0.00000029 \ p_0$ (atm.). Since $1/\epsilon = T_0$, the absolute temperature of melting ice can be calculated from measured expansion coefficients.

In Table I are given the measured values of ϵ_p , and calculated values of T_0 . In Table II are the measured values of ϵ_p and calculated values of T_0 .

It is seen from these tables that in no way can the above data be averaged to give a value of 273.20 as the ice point on the absolute centigrade scale as obtained by Henning and Heuse. The data of Henning and Heuse on nitrogen vary from an ice point of 273.130 to one of 273.231.

⁹ In Keyes' paper, This Journal, 43, 1461 (1921), there is a typographical error in this equation, the square term in the denominator of the expression in brackets being omitted.

An average of their data alone, however, gives 273.175°. A consideration of the other data leads one to believe that even this is too high by several hundredths of a degree. Keyes, 5 after a review of the data on coefficients

Table I

Absolute Ice-Point Temperatures Computed from Measured Constant Pressure
Expansion Coefficients

þ (atm.)	Therm. material	$\epsilon_p \times 10^3$ (obs).	€(calc.)	Te(calc.)
1.318	Pt Ir	3.67315°	3.66121	273.134
1.825	Pt Ir	3.67775°	3.66123	273.132
0.520	Quartz	3.66561 ^b	3.66090	273.157
0.546	Quartz	3.66587 ^b	3.66093	273.155
1.042	Quartz	3.67005^{b}	3.66061	273.179
1.032	Quartz	3.67019^{b}	3.66085	273.161
0.996	Quartz	3.66991	3.66089	273.158
0.289	59 ^{III} glass	3.6630°	3.66038	273.196
0.671	59 ^{III} glass	3.6679°	3.66082	273.163
1.460	59 ^{III} glass	3.6742°	3.66098	273.151

Mean of above values gives for T_0 , 273.159.

° Ref. 7.

Absolute Ice-Point Temperatures Computed from Measured Constant Volume Expansion Coefficients

		Therm.				
	⊅ (atm.)	material	$\epsilon_v imes 10^3$	Observer	e(calc.)	$T_{\mathfrak{o}(\mathrm{calc.})}$
	1.044	verre dur	3.6718	Chappuis (1902)	3.66210	273.067
	0.698	verre dur	3.6685	Chappuis (1902)	3.66202	273.073
	1.310	Pt Ir	3.6747	Chappuis (1887)	3.66253	273.035
	1.318	Pt Ir	3.6744	Chappuis (1907)	3.66215	273.064
	0.742	Quartz	3.6699	Chappuis (1914)	3.66301	273.000
	0.727	Quartz	3.66943	Chappuis (1914)	3.66267	273.025
	0.740	Quartz	3.66959	Chappuis (1914)	3.66272	273.021
	0.413	Pt	3.665	Day and Clement	3.66116	273.137
	0.724	Pt	3.668	Day and Clement	3.66128	273.129
	0.979	Pt	3.670	Day and Clement	3.66091	273.156
	1.2961	Pt	3.673	Day and Clement	3.66095	273.153
	0.8305	59 ¹¹¹ glass	3.6706	Holborn and Henning	3.66288	273.009
	0.8175	59 ^{III} glass	3.6699	Holborn and Henning	3.66231	273.052
	0.8166	Quartz	3.66843	Holborn and Henning	3.66085	273.161
	0.2895	59 ^{III} glass	3.6626	Henning and Heuse	3.65991	273.231
٠	0.6710	59 ^{III} glass	3.6675	Henning and Heuse	3.66126	273.130
	1.4605	59 ^{III} glass	3.6752	Henning and Heuse	3.66062	273.178
	0.800	Quartz	3.6687	Keyes, Townshend, Young	3.66127	273.129

Mean of the above gives $T_0 = 273.097$; omitting Chappuis' values, $T_0 = 273.134$; average of all nitrogen data gives $T_0 = 273.119$.

of expansion for all gases for which data are available, reached the conclusion that $T_0 = 273.14$. Buckingham decided on 273.13. From the above data it is evident that 273.12° is about as good a value as can be

^a Ref. 1. ^b Ref. 4.

obtained from the nitrogen coefficients alone. A paper will soon be forth-coming from this Laboratory dealing with the data on other gases, but for the present it appears that 273.13° is about as good a value for T_0 as can be decided upon.

In conclusion it is desired to thank Dr. Keyes for his valuable suggestions and assistance.

Summary

The value of T_0 , the absolute temperature of melting ice, from the nitrogen volume and pressure expansion coefficients gives a mean value of 273.12° . The mean value obtained by using the data of other gases including the Joule-Thomson coefficient is $273.13^{\circ} \pm .01^{\circ}$.

CAMBRIDGE 39, MASSACHUSETTS

[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 29]

THE CRYSTAL STRUCTURE OF POTASSIUM HYDROGEN FLUORIDE

By Richard M. Bozorth Received June 25, 1923

Introduction

Crystals of potassium hydrogen fluoride, KHF₂, were prepared by the spontaneous evaporation at room temperature of an aqueous solution of potassium fluoride and hydrofluoric acid. They are known¹ to belong to the tetragonal system and to have an axial ratio a: c = 1:0.601.

The X-ray data were obtained (1) from photographs of line spectra from the principal planes, using rhodium as the target, and (2) from two Laue photographs taken with the beam approximately perpendicular to the (001) planes. The methods of analysis and treatment are the same as those previously employed.²

The Unit of Structure

The data from the spectral photographs are given in Table I; d is the interplanar distance expressed in Ångstrom units and n the order of reflection. The wave length of the rhodium $K\alpha_1$ line was taken to be 0.6121 Å., and that of the unresolved $K\alpha$ line to be 0.614 Å.

Combining the values of d/n with the density of the crystals, determined by a suspension method to be 2.37, it was found that the data are consistent with a unit containing 1 molecule of KHF₂. Examination of the Laue photographs, however, showed that many values of $n\lambda$ calculated for this unit by means of the well-known Bragg equation were smaller

P. Groth, "Chemische Krystallographie," Engelman, Leipzig, 1906, vol. 1, p. 312.
 Bozorth, This Journal, 44, 317 (1922); 44, 2232 (1922). See also Wyckoff, Am. J. Soi., [5] 1, 127 (1921) and Dickinson, This Journal, 44, 276 (1922).

than any wave lengths that could be present at the voltage applied to the X-ray tube, which was about 53,000 volts. The smallest unit that would avoid this difficulty was found to have the dimensions 5.67 imes 5.67×6.81 Å., so this unit was considered to be the true one. The axial ratio is therefore 1.201, and the distance between any two adjacent hkl

		Table I	
А	EROM	THE SPECTRAL	PHOTOGRAPHS

	DA'	ra from th	e Spectral	PHOTOGRAPHS	
Reflecting plane	Angle of reflection	Spectral line	d/n	Estimated intensities	Calculated structure factor
(001)	(5°)	α_1	(3.5)	Extremely weak	4
	10° 21′	$lpha_1$	1.703	Very strong	148
	15° 39′	α_1	1.135	Extremely weak	4
(110)	4° 23′	α	4.016	Medium strong	47
	8° 48′	α	2.007	Medium	79
	13° 19′	α	1.333	Very weak	21
	17° 50′	α	1.002	Weak	138

planes is 5.67 $(h^2 + k^2 + 0.685 l^2)^{-\frac{1}{2}}$ Å. The density calculated for this unit containing 4KHF2 is 2.35.

The Possible Arrangements

The symmetry of the Laue photographs corresponds to the point group D_{4h}; accordingly, only space groups were considered which are isomorphous with the point groups V_d, C_{4v}, D₄, and D_{4h}. Furthermore, since all the planes reflecting in the first order on the Laue photographs were found to have one index even and two indices odd, it was concluded that the underlying lattice was the body-centered one, and the space groups were considered accordingly.

It was observed (see Table I) that reflections from the (001) planes were extremely weak in the second and sixth orders, and very strong in the fourth order, while odd orders were absent. It seemed reasonable, therefore, to suppose that in the fourth order all the atoms are reflecting in phase, while in the second and sixth order the potassium atoms act in opposition to the fluorine atoms. Therefore, the arrangements were limited to those which place the fluorine atoms in planes 1/2d(001) apart, and the potassium atoms in planes midway between the fluorine atoms. There are three such arrangements³ for the fluorine atoms, as follows.

- $\begin{array}{ll} (1) & u,\frac{1}{2}+u,0; \; \bar{u},\frac{1}{2}-u,0; \; \frac{1}{2}-u,u,0; \; \frac{1}{2}+u,\bar{u},0; \; \frac{1}{2}+u,u,\frac{1}{2}; \; \frac{1}{2}-u,\bar{u},\frac{1}{2}; \; u,\frac{1}{2}-u,\frac{1}{2}; \; \bar{u},\frac{1}{2}+u,\frac{1}{2}. \\ (2) & u00; \; \bar{u}00; \; 0u0; \; 0\bar{u}0; \; \frac{1}{2}+u,\frac{1}{2},\frac{1}{2}; \; \frac{1}{2}-u,\frac{1}{2},\frac{1}{2}; \; \frac{1}{2},\frac{1}{2}+u,\frac{1}{2}; \; \frac{1}{2},\frac{1}{2}-u,\frac{1}{2}. \\ (3) & uu0; \; \bar{u}\bar{u}0; \; \bar{u}\bar{u}0; \; \bar{u}\bar{u}0; \; \frac{1}{2}+u,\frac{1}{2}+u,\frac{1}{2}; \; \frac{1}{2}-u,\frac{1}{2}+u,\frac{1}{2}; \; \frac{1}{2}+u,\frac{1}{2}-u,\frac{1}{2}; \; \frac{1}{2}-u,\frac{1}{2}+u,\frac{1}{2}. \end{array}$

There are two such ways of placing the potassium atoms with respect to the fluorine atoms, namely,

$$\begin{array}{l} (1) \ 0 \ 0^{1}/_{4}, \ 0 \ 0^{3}/_{4}, \ ^{1}/_{2} \ ^{1}/_{2} \ ^{1}/_{4}, \ ^{1}/_{2} \ ^{1}/_{2} \ ^{3}/_{4}. \\ (2) \ 0 \ ^{1}/_{2} \ ^{1}/_{4}, \ 0 \ ^{1}/_{2} \ ^{3}/_{4}, \ ^{1}/_{2} \ 0 \ ^{1}/_{4}, \ ^{1}/_{2} \ 0 \ ^{3}/_{4}. \end{array}$$

³ Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Inst. Pub., 318 (1922).

Determination of the Structure

The six ways of arranging the potassium and fluorine atoms were investigated for all values of the parameter u; and it was shown on the basis of qualitative comparisons of intensities of Laue spots that the only arrangement consistent with the data is the combination of (1) for potassium with (1) for fluorine. The intensity data chiefly used in arriving at this conclusion are: $(2\overline{5}1) > (\overline{4}31)$, $(\overline{56}1) > (\overline{7}01)$, $(\overline{56}1) > (\overline{27}1)$, $(\overline{92}3) > (\overline{7}01)$, $(\overline{92}3) > (\overline{38}3)$, $(7\overline{3}4) > (\overline{7}32)$, $(5\overline{7}4) > (\overline{57}2)$. The value of the parameter u in the correct arrangement was determined from these and other intensity comparisons to be 0.14, with an estimated maximum error of 0.01. The data from one Laue photograph are given in Table II. The reflections are in the second order when a 2 is prefixed to the indices of the reflecting plane; otherwise they are in the first order. The last columns in both tables give the structure factor calculated for the correct arrangement when u is 0.14.

TABLE II
DATA FROM ONE OF THE LAUE PHOTOGRAPHS

Reflect- ing plane	Inter- planar distance ÷ n	Wave Ir length of X-rays		Calcu- lated tructure factor	Reflect- ing plane	Inter- planar distance + n		Intensity of spot	Calcu- y lated structure factor
(310)	1.79	0.34	2.5	116	(714)	0.73	0.43	0.1	30
(141)	1.35	.35	0.2 -	20	(554)	.73	.41	. 2	69
$2(\overline{2}\overline{1}0)$	1.27	. 41	2.5	89	(732)	.73	43	.05	13
(431)	1.12	.47	0.07 -	13	2(232)	.72	.40	05	40
(510)	1.11	. 33	0.6	90	$(\bar{5}\bar{6}1)$.72	. 39	.02	58
$(5\bar{1}2)$	1.06	.44	1.3	62	$2(0\overline{4}1)$.70	. 43	.05	24
(251)	1.04	.42	0.8	67	(563)	. 69	. 43	.05	58
(530)	0.97	.32	0.1	56	$(7\bar{3}4)$. 69	.45	. 4	139
$(5\overline{3}2)$	0.94	.41	1.0	96	(743)	. 67	.48	.00	3
(161)	0.92	.40	0.1	47	2(331)	. 66	. 47	.05	55
2(131)	0.89	.36	0.3	83	(572)	.65	45	.05	54
(613)	0.86	.42	0.1	47	$2(\bar{1}42)$. 64	.40	.02	66
(361)	0.84	.46	0.05 -	29	$(3\bar{8}3)$.64	.42	.00	24
(701)	0.80	.40	0.00	0	$-2(\overline{4}\overline{2}1)$.62	.43	. 1	125
(552)	0.78	.39	0.3	83	(574)	.62	46	. 1	98
(172)	0.78	49	0.8	122	(912)	. 62	.39	.05	73
$(\bar{2}\bar{7}1)$	0.77	.39	0.00	9	$(9\bar{2}3)$. 59	.48	.02	71

For the comparison of intensities, planes may be divided into two classes: (1) those having the last index odd and reflecting in the first order; (2) all other planes. This classification is such that the intensities of the reflections from planes of Class 1 depend only on the reflecting power of the fluorine atoms, while those from Class 2 planes depend on both kinds of atoms. Intensities were calculated in the usual manner, assuming the reflecting powers of the atoms to be proportional to their atomic numbers; however, when only qualitative comparisons are made involving planes of the same class, the validity of comparing calculated intensities with observation is dependent only on the assumption that the reflecting power of the potassium atom is approximately as great as or greater than twice the reflecting power of the fluorine atom.

Discussion of the Structure

The structure is represented diagrammatically in Fig. 1. It may be regarded as an ammonium chloride arrangement of potassium atoms and fluorine dumb-bells. The arrangement may be derived from any of the space groups D_{4h}^{18} , V_{0}^{10} , and D_{4}^{9} . For the hydrogen atoms the only positions consistent with the symmetry are (1) 00u; $00\bar{u}$; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ + u; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ + u; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ 0 $\frac{1}{2}$ 0, $\frac{1}{2}$ 0 0, $\frac{1}{2}$ 0 $\frac{1}{2}$ 1, 0 $\frac{1}{2}$ 1, 0 $\frac{1}{2}$ 1, 0 $\frac{1}{2}$ 1, 0 $\frac{1}{2}$ 3, 1 $\frac{1}{2}$ 0 $\frac{3}{4}$. Of these the first may be discarded; for, if the hypothesis of constant atomic radii is even approximately correct, there is not room for the hydrogen atoms between potassium atoms that are 3.41 Å. apart.

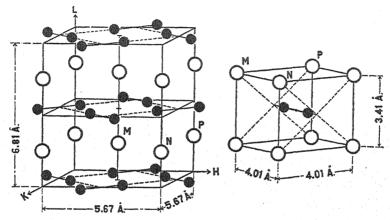


Fig. 1.—The arrangement of the atoms in KHF₂. The potassium atoms are represented by the larger circles and the fluorine atoms by the smaller ones. The larger tetragonal prism represents a complete unit of structure containing 4 KHF₂. The smaller prism contains one KHF₂ and is related to the larger in the way indicated by the letters M, N and P; it shows how the structure is similar to that of ammonium chloride, the K atoms corresponding to N atoms and the F dumb-bell corresponding to Cl atoms

The second arrangement places each hydrogen atom between 2 fluorine atoms that are 2.24 Å. apart, and forms what may be considered an $\mathrm{HF_2}^-$ ion. If the radius 4 0.62 Å. be assigned to the fluorine atom, the radius of the hydrogen atom in this position is 0.50 Å. The third possible position for hydrogen leaves the fluorine atoms much farther apart than the radius usually ascribed to them permits, but permits the same unusually large distances between adjacent negative atoms observed in cadmium iodide, stannic iodide, and molybdenum disulfide.

The distances in Angstrom units between the atoms are given in Table

- 4 Wyckoff, Proc. Nat. Acad. Sci., 9, 33 (1923).
- ⁵ Ref. 2, p. 2232.
- 6 Dickinson, This Journal, 45, 958 (1923).
- ⁷ Dickinson and Pauling, ibid., 45, 1466 (1923).

III, where they are compared with the corresponding distances in potassium fluoride.8

Table III

THE DISTANCES BETWEEN THE ATOMS

		K and K	
In KHF ₂	2.77	$\int 3.41$, 2.25
		₹ 4.01 €	
In KF	2.68	3.79	

Summary

The positions of the potassium and fluorine atoms in tetragonal potassium hydrogen fluoride, KHF₂, have been determined by means of X-rays. The dimensions of the unit are $5.67 \times 5.67 \times 6.81$ Å. The structure may be described as an ammonium chloride arrangement of potassium atoms and fluorine dumb-bells, the two atoms of each dumb-bell lying in a plane perpendicular to the tetragonal axis. For the hydrogen atoms there are two possible positions, one of which is in the middle of the dumb-bell, forming an HF₂-ion. The distances in Ångstrom units between the atoms are summarized in Table III.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM SANDERS CHEMICAL LABORATORY, VASSAR COLLEGE]

THE STABILITY OF SODIUM THIOSULFATE SOLUTIONS

By Martin Kilpatrick, Jr., and Mary L. Kilpatrick

Received June 27, 1923

The present investigation was undertaken as a critical study of the stability of $0.01\ N$ sodium thiosulfate under the conditions of its use as a standard solution in an analytical laboratory. It was also hoped that the investigation might throw some light on the mechanism of the decomposition.

Topf¹ in 1887 proved that the carbon dioxide of the air could not account for the deterioration, and concluded that it was to be attributed to direct oxidation: $Na_2S_2O_3 + O \longrightarrow Na_2SO_4 + S$. He also noticed that the fall in normality was greater in summer than in winter. Kolthoff² made an extensive study of the behavior of $0.1\ N$ and $0.01\ N$ sodium thiosulfate solutions under various conditions and in the presence of a great number of substances. He found that sunlight hastened the decomposition; that $0.01\ N$ solutions decomposed much more rapidly than $0.1\ N$; that small amounts of mercuric iodide greatly retarded the decomposition, as did small amounts of alkaline substances; that salts of the heavy metals

⁸ Wyckoff, J. Washington Acad. Sci., 12, 251 (1922).

¹ Topf, Z. anal. Chem., 26, 137 (1887).

² Kolthoff, Pharm. Weekblad, 56, 878 (1919); Z. anal. Chem., 60, 344 (1921).

had various effects; that the sulfur deposit from decomposed thiosulfate solutions accelerated the decomposition, and that carbon dioxide had little influence. He suggested that the decomposition might be due to certain sulfur-consuming microörganisms. He recommended that in preparing the solution 10 mg. of mercuric iodide or 200 mg. of sodium carbonate be added per liter, and that the flasks be sealed and kept in the dark.

Rice, Kilpatrick and Lemkin³ studied the behavior over a period of 52 days of $0.01\ N$ solutions of sodium thiosulfate made up with different grades of distilled water. Using the same method of analysis, the authors have continued this study for some 200 days. The results, which in general are similar to those already given, are summarized in the following table.

Table I
Effect of Different Grades of Distilled Water

	Distilled water	Initial titer, Oct. 3, 1922 N	Final titer, May 31, 1923 N	Fall
1	Laboratory	0.012401	0.009848	20.6
2	Redistilled	.013248	.011810	10.9
3	Redistilled, freshly boiled	.014085	.014016	[0.5]
4	Redistilled, through which CO ₂ -free			
	air had been bubbled	.013111	.012866	1.9

At the same time a fifth bottle was prepared in the same way as in Expt. 1, was sealed, and set aside. Six months later it was opened, fitted with a soda-lime tube and siphon, and a portion was analyzed in the usual way. The normality was found to be 0.012688. In 40 days the normality dropped to 0.012512, a decrease of 1.4%. This is distinctly at variance with the result reported by Treadwell⁴ for a $0.1\ N$ solution.

During the period of investigation, portions were drawn off from the bottles for other experiments. At the end of the work the air spaces above the solutions varied from 4 to 10 liters. (We mention this because it would be the usual case in the laboratory.) Considerable deposits of sulfur formed in Bottles 1, 2 and 5, while no deposit was apparent in 3 or 4. The hydrogen-ion concentration of the solutions, determined colorimetrically from time to time, showed no appreciable change.

The most stable of the solutions, 3, was selected for the purpose of testing the effects of carbon dioxide, of oxygen, and of small quantities of alkali on the titer of $0.01\,N$ sodium thiosulfate solution. Portions of the solution through which carbon dioxide and oxygen, respectively, had been bubbled for several hours were siphoned into glass-stoppered tubes. At intervals a tube was opened and its contents analyzed. In the case of the alkali, a weighed amount of standard sodium hydroxide solution was added to

³ Rice, Kilpatrick and Lemkin, This Journal, 45, 1361 (1923).

⁴ Treadwell-Hall, "Analytical Chemistry," Wiley and Sons Co., fifth ed., 1919, vol. 2, p. 645.

a weighed amount of thiosulfate, and the resulting solution, 0.001 N in sodium hydroxide, was siphoned into tubes, as before. The analysis of the alkaline solution was carried out in a slightly different manner. As Kolthoff⁵ has pointed out, in 0.01 N solution the minimum hydrogen-ion concentration at which iodine oxidizes thiosulfate quantitatively to tetrathionate is 3.16×10^{-7} ; at lower concentrations of hydrogen ion the thiosulfate is partially oxidized to sulfate. Kolthoff showed that the error is much less when the thiosulfate is titrated with iodine than in the reverse procedure. In his work with slightly alkaline thiosulfate, Kolthoff ran the thiosulfate into an excess of acidified iodine and titrated back with thiosulfate. In the present investigation the thiosulfate was run into a suitable buffer and was titrated directly with iodine. The results of the experiments are given in Table III. For purposes of comparison, data for the original solution over the same period are included.

Table II Effects of Carbon Dioxide, of Oxygen and of Sodium Hydroxide

Date		Original solution No. 3	Solution treated with CO ₂ on Mar. 3 N	Solution treated with O ₂ on Feb. 27 N	Solution 0,001 N in NaOH; prepared Feb. 28 N
Mar.	3	0.014005	0.014020	0.013998	(0.013938, calc.)
1	0		.014035	.013987	
1	7	.014014			.013944
2	8	.014005	.014035	.013995	.013931
Apr. 2	8	.014013	.014028	.013955	.013910

It is evident that carbon dioxide, oxygen and sodium hydroxide have very little effect on a stable solution of sodium thiosulfate. The slight effect observed in the case of carbon dioxide is in agreement with the results of Topf and of Kolthoff. It is, however, contrary to the results of Hahn and Windisch, who report an increase of 10% over a period of 51 days in the normality of a 0.02~N solution of sodium thiosulfate, half saturated with carbon dioxide. The same authors, however, report a gain of approximately 9% for a 0.02~N solution of sodium thiosulfate in distilled water. As far as we know, only one other such case appears in the literature, that of Waterman.

During the course of these experiments, a bacteriological examination revealed the fact that the bacterial count of all the solutions was high, and that the solution which was decomposing most rapidly, No. 1, contained by far the greatest number of organisms. In addition, it appeared to give a pure culture. The organism was isolated, as was another organism from Solution 2. Two sterilized portions of Solution 4 were inoculated with these organisms and were kept at 21° for 24 hours. One-cc.

⁵ Kolthoff, Pharm. Weekblad, 56, 572 (1919).

⁶ Hahn and Windisch, Ber., 55, 3163 (1922).

⁷ Waterman, Chem. Weekblad, 15, 1098 (1918).

portions of the inoculated solutions were added to 500-600 cc. of Solution 4 in 2 glass-stoppered liter bottles. The following table shows the changes in normality observed in a month's time.

Table III Changes in Normality in One Month's Time

Date	600 cc. of Soln. $4+1$ cc. inoculated with bacteria from Soln. 1	600 cc. of soln. 4 + 1 cc. inoculated with bacteria from Soln. 2
Apr. 1	1 0.012934	0.012934
1	8 .012921	.012931
May	2 .012284	.012872
1	2 .011848	.012716
	Fall, 8.3%	Fall, 1.6%

During the same period the normality of the original solution, 4, decreased by 0.3%. It is evident that the decomposition is due to the action of bacteria.

The authors wish to thank Dr. E. M. Twiss of Vassar College for her help with the bacteriological work.

Summary

The stability of several $0.01\ N$ solutions of sodium thiosulfate has been studied over a period of 8 months.

Freshly boiled redistilled water gave a solution that was more permanent than that obtained with laboratory distilled water, ordinary redistilled water or redistilled water through which carbon dioxide-free air had been bubbled.

Carbon dioxide, oxygen or dilute sodium hydroxide had very little effect on the stability of the solution.

Decomposition is caused by the action of bacteria.

POUGHKEEPSIE, NEW YORK

NOTE

A Glass-to-Metal Joint.—In a recent note by Merle L. Dundon¹ on a glass-to-metal joint it was claimed that the method of McKelvy and Taylor² of platinizing, copper plating and soldering was tried without success. The failure of the joints by cracking of the glass upon cooling was ascribed to heat strains introduced by the soldering process. Heat strains may be introduced during the platinizing process, if the glass is not cooled carefully, but the temperature of melted tin is not sufficiently

- 8 The organism isolated from Solution I has been identified by Selman A. Waksman, at the New Jersey Agricultural Experiment Station, as *Thiobacillus thioparus*. Its characteristic reaction is the transformation of thiosulfate into sulfate and elementary sulfur.
 - ¹ Dundon, This Journal, 45, 716 (1923).
 - ² McKelvy and Taylor, ibid., 42, 1364 (1920).

high to introduce permanent strains in glass. The only permanent strains introduced in soldering glass to metal joints are due to the fact that a metal with a greater expansion coefficient is shrunk on the glass by cooling. Although the soda glass used by the writer has very seldom cracked upon cooling, Pyrex glass, which has a smaller expansion coefficient, has frequently cracked unless the joint was a small one or the metal part was made very thin so that it stretched instead of cracking the glass. These facts lead one to suspect that Dundon used a glass that contained numerous heat strains originally or which had an expansion coefficient unusually small for soda glass.

The writer has made several platinized soldered joints, but has found that equally satisfactory joints can be obtained by the use of tin or low melting-point solder without platinizing the glass, a method also mentioned in the article by McKelvy and Taylor.

When joints are made without platinizing, both the glass and metal must be very clean. The following procedure has been successful. The glass is cleaned with chromic acid, rinsed with distilled water and dried; the metal part is coated with tin or solder and the surface of the melted tin cleaned with a solution of zinc chloride. The metal part is allowed to cool, is washed thoroughly with distilled water, and if necessary is scrubbed with absorbent cotton or other material free from grease or dirt, and dried. Then the two parts are held together above a flame and as soon as the tin melts, the glass is inserted in the metal without the addition of any flux. When one part is fixed on an apparatus, it may be inconvenient to use a torch, in which case a soldering copper just hot enough to melt the tin may be held to the outside of the metal part and the glass pushed in slowly as the tin melts.

One joint about 5 mm. in diameter has withstood the vapor pressure of liquid carbon dioxide (60 to 70 atmospheres) for 3 years. A joint 41 mm. in diameter, tested with a pressure difference of about 1 atmosphere, was made with a solder melting at 130°. The first attempt was a failure because the flame came into direct contact with the glass and cracked it. Success was attained in the second attempt, however, when precautions were taken to keep the flame from striking the glass. No trouble arose from the fact that the glass did not fit tightly in the metal.

The copper-plated joint mentioned by Dundon is probably satisfactory for moderate pressures, but the process of manufacture requires much more time and labor than for the soldered joint.

BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D. C. Received April 6, 1923 CYRIL H. MEYERS

[CONTRIBUTION FROM THE OFFICE OF PLANT PHYSIOLOGICAL AND FERMENTATION INVESTIGATIONS, WITH THE COÖPERATION OF THE OFFICE OF CEREAL INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE OCCURRENCE OF POLYPEPTIDES AND FREE AMINO ACIDS IN THE UNGERMINATED WHEAT KERNEL

By S. L. Jodidi and K. S. Markley Received April 23, 1923

Introduction

While we know, from the work of Osborne¹ and his associates, that the wheat kernel contains 5 proteins, we are altogether inadequately informed, to say the least, in regard to the nitrogenous constituents other than the proteins. According to Schulze² the non-protein nitrogenous compounds present in the seed of wheat make up 0.240% calculated on the basis of the dry seed, or 11.2% calculated on the basis of its total nitrogen.

Frankfurt³ is doubtful with regard to the occurrence of amino acids in the wheat embryo, since his attempts to show their presence in alcoholic extracts of the embryo have led to negative results.

Richardson and Crampton⁴ reported the presence of allantoin—a purine derivative in the wheat embryo, while Frankfurt³ showed the occurrence of the bases betaine and choline.

These results were confirmed by the work of Schulze,⁵ who also reported the presence of asparagine in the wheat embryo, stating, however, that the quantity of those nitrogenous compounds is quite insignificant when related to the weight of the seed. Later Schulze⁶ and Castoro reported the occurrence of arginine also, in the embryo, adding that its quantity is very small. In more recent work by Grindley⁷ and his associates as well as by Nollau⁸ very complete estimations of the amino acids in wheat, wheat bran and gluten were reported. Their data, however, refer to hydrolyzed wheat and its by-products.

No mention is made in the literature of the occurrence of polypeptides in the wheat kernel, as far as we are aware, despite the fact that they were discovered and described by Fischer⁹ some 20 years ago. However, from the results reported in the experimental part of this paper it will be seen that the 4 wheat varieties investigated showed the presence of considerable quantities of free amino acids and polypeptides in the ungerminated wheat kernel.

- 1 Osborne, "The Proteins of the Wheat Kernel," Carnegie Inst. Pub., 1907.
- ² Schulze, Z. physiol. Chem., 41, 455 (1904).
- ³ Frankfurt, Landw. Vers.-Sta., 47, 456 (1896).
- ⁴ Richardson and Crampton, Ber., 19, 1181 (1886).
- ⁵ Schulze, Chem.-Ztg., 18, 799 (1894).
- 6 Ref. 2, p. 467.
- ⁷ Grindley, This Journal, 37, 2762 (1915); 45, 815 (1923).
- ⁸ Nollau, J. Biol. Chem., 21, 611 (1915).
- ⁹ Fischer, "Untersuch. über Aminosäuren, Polypeptide und Proteine," J. Springer, Berlin, 1906.

Experimental Part

For our work we have selected the wheat varieties Fultz, Marquis, Kubanka, and Kanred, because of their commercial importance. Fultz¹⁰ represents a soft red winter wheat which is widely raised in the eastern half of the United States. Marquis,¹⁰ introduced into this country from Canada in 1913, has become the leading variety of hard red spring wheat. Kubanka¹⁰ is a widely grown commercial variety of durum wheat, usually outyielding the hard red spring wheats in the northern Great Plains because of its greater resistance to drought and rust. Kanred,¹¹ a pure-line selection from a wheat introduced into the United States from Russia in 1900, is a hard red winter variety extensively grown in the central Great Plains area.

For the experimental work the wheat samples were ordinarily ground in an electric buhr-mill to pass a 40-mesh sieve. Inasmuch as the results in this paper are largely based on the total and the protein nitrogen of the different wheat varieties a number of estimations, including ammoniacal nitrogen, were made. The average of these was taken as a basis for the calculations. It may be mentioned here that the *protein nitrogen* was estimated according to Stutzer's method outlined elsewhere, 12 while the ammoniacal nitrogen was determined in a vacuum according to Grafe's 13 method.

The results obtained are presented in Table I.

Table I
Proportion of Total, Protein and Ammoniacal Nitrogen in the Ungerminated
Wheat Kernel

		** 111921 .	*****			
	Total nitrogen		ı nitrogen	nitro	oniacal ogen	
Variety of wheat	Oven- dried wheat	Oven- dried wheat %	Total nitrogen	Oven- dried wheat %	Total nitrogen	
Fultza (C. I. 3598)	1.80	1.64	91.76	0.0026	0.142	
	± 0.03	± 0.003	± 0.22	$\pm .0004$	$\pm .023$	Av. dev.
Kanred ^b (C. I. 5146)	2.83	2.47	87.01			
	± 0.01	± 0.04	± 1.31			Av. dev.
Kubanka ^c (C. I.)	3.03	2.73	86.73	.0033	.109	
	± 0.03	± 0.02	± 0.76	$\pm .0003$	$\pm .01$	Av. dev.
Marquis ^d (C. I. 3641)	3.04	2.65	87.26	.0033	.109	
	± 0.03	± 0.04	± 1.29	$\pm .0004$	$\pm .012$	Av. dev.

^a From the Arlington Farm, Roslyn, Va.; 1920.

^b From the Hays Branch Expt. Sta., Hays, Kansas; 1922.

c 1920.

^d From the Dickinson Sub-Station, Dickinson, N. D.: 1920.

¹⁰ Clark, Martin and Ball, U. S. Dept. Agr. Bull., 1074 (1922); U. S. Dept. Agr. Farmers' Bull., 1280, 1281, 1301 (1922); 1304 (1923).

¹¹ U. S. Dept. Agr. Circ., 194 (1921).

¹² Jodidi, Moulton and Markley, This Journal, 42, 1063 (1920).

¹³ Grafe, Z. physiol. Chem., 48, 300 (1906).

In looking over Table I, in which the average is based in each case on at least three determinations, it will be noticed that the differences in the total nitrogen of the several varieties are rather marked and characteristic, the nitrogen percentage of Fultz being lowest (1.80), that of Kanred considerably higher (2.83), and that of Kubanka and Marquis higher than either of the others (3.03 and 3.04, respectively).

As to the protein nitrogen, the differences between the varieties when calculated to the oven-dried wheat follow about the order indicated in the case of the total nitrogen. However, when the protein nitrogen is referred to the total nitrogen we find that the differences between Kanred (87.01), Kubanka (86.73), and Marquis (87.26), are comparatively small, only Fultz showing a higher percentage (91.76).

With regard to the proportion of the ammoniacal nitrogen, which was estimated because it is formol-titrable along with the amino acids, it will be seen that the differences between the varieties are small, the total proportion of ammoniacal nitrogen for the three varieties examined being generally quite insignificant.

After a few preliminary experiments the methods finally adopted, in order to demonstrate the presence of amino acids in the wheat seed, were as follows.

Several flasks each containing 25 g. of "whole wheat" flour and 400 cc. of distilled water were shaken at room temperature for 2 hours and the contents filtered at once. The residue on the filter contained the undissolved substance, the bran, starch, etc. The clear filtrate, which was apparently free from starch, was concentrated on the waterbath. During evaporation, precipitates formed that displayed the xanthoprotein and biuret reactions and otherwise appeared to consist chiefly of proteins. These precipitates were separated by centrifugation. The supernatant liquid was evaporated on the water-bath to dryness and the residue extracted with 70% alcohol in order to remove the rest of protein and the residue—a yellow sirup—dissolved readily in hot water. The solution was made up to 100 cc., of which 2 portions of 20 cc. each were oxidized according to Kjeldahl's method to ascertain the quantity of nitrogen present. Of the remaining solution, 50 cc. was freed from carbon dioxide, phosphoric acid and coloring matter, and titrated with formol according to Sörensen's method as applied by one'r of us elsewhere (Method A).

The flour extracts ordinarily showed a neutral or a very slightly acid reaction. The probability that the slight acidity could have a hydrolyzing effect upon the nitrogen compounds in the flour extracts seemed to be quite remote. However, in order to remove any doubt the experiment was repeated with the difference that all evaporations took place under reduced pressure. We refer to this modification as Method B.

While operations incidental to the two foregoing methods remove the proteins, they do not accomplish it quantitatively. Inasmuch, however, as proteins containing ly-

¹⁴ Except gliadin, which is soluble in the alcohol.

¹⁵ The very small residue on the filter displayed protein reactions due undoubtedly to some gliadin present.

¹⁶ Sörensen, Biochem. Z., 7, 48 (1907).

¹⁷ Jodidi, This Journal, 33, 1236 (1911); 34, 98 (1912); 40, 1031 (1918).

sine, as is the case with glutenin and leucosin occurring in the wheat kernel, have been shown to contain free amino groups which are formol-titrable, 18 the complete removal of the proteins from the aqueous solutions prior to their titration with formol seemed necessary. Method A, therefore, was modified as follows. The dried alcoholic extract of the flour was dissolved in hot water, the solution brought to boiling, carefully acidified with acetic acid, boiled for a few minutes and filtered. To the filtrate freshly prepared lead hydroxide¹⁰ and some lead acetate were added. The mixture was boiled for a few minutes and filtered. The clear filtrate was then concentrated on the water-bath to 100 cc. and treated as outlined in Method A. We refer to the results secured in this way as those of Method C. To do away with any possible changes due to evaporation under ordinary pressure, Method C was further modified so as to concentrate the extracts in a vacuum. This modification is referred to as Method D. For lack of material however, not all four methods could be applied to each variety. Since the reaction of amino acids with formaldehyde is reversible according to the equation, NH₂RCOOH+ CH₂O CH₂ = NRCOOH + H₂O, excess of formaldehyde was applied to make sure that the forward reaction takes place quantitatively. The results obtained are recorded in Table II.

TABLE II
PROPORTION OF AMINO ACID NITROGEN IN THE UNGERMINATED WHEAT KERNEL

Variety of wheat		d dried		Total nitrogen	Water- soluble nitrogen	Variety of M wheat a	[ethod	dried	Air- dried n	trogen	Water- soluble nitrogen
	(A	0.033	0.029	1.85	11.13		A	0.047	0.043	1.55	11.41
Fultz	₹B	.029	.026	1.61	9.72	Kubanka	B	.037	.034	1.21	8.92
	l c	.033	.029	1.85	11.12		D	.039	.036	1.28	9.41
	A	.048	.043	1.56	10.09	77	B	.066	.059	2.32	16.04
Marquis	B	.060	.054	1.95	12.63	Kanred	D	.067	.060	2.38	16.46
	D	. 055	.050	1.81	11.67		•				

The most outstanding feature of the results in Table II, in which the figures represent the average of at least two estimations, seems to us to be the fact that each of the four methods applied, while differing from the others to a certain extent, indicates appreciable quantities of amino acids, the proportions (in round figures) for Kubanka, Fultz, Marquis, and Kanred being respectively 10, 11, 11, and 16% of amino acid nitrogen calculated to the water-soluble nitrogen, and 1.4, 1.8, 1.8, and 2.3%, calculated to the total nitrogen.

Concerning acid amides, it is true that asparagine was reported by Schulze⁶ and Castoro as well as by Frankfurt²⁰ to occur in the wheat embryo. However, these authors failed to give information as to the varieties in which it occurs, nor did they give the percentage in which it is present. It was, therefore, deemed of sufficient interest to obtain data on those subjects. The way we proceeded was as follows.

The alcoholic extract of a definite quantity of flour prepared as described in Method A was freed from alcohol by distillation. The residue was taken up with water and made

¹⁸ Z. physiol. Chem., 81, 274 (1912).

¹⁹ Hoppe-Seyler, "Handbuch der Physiologisch-Pathologisch Chemischen Analyse," A. Hirschwald, Berlin, 1909, p. 393.

²⁰ Ref. 3, p. 453.

up to 100 cc. Of this solution 2 portions of 20 cc. each were oxidized according to Kjeldahl's method to find out the quantity of nitrogen present. To 50 cc. of the remaining solution hydrochloric acid was added to a concentration of 20% and the whole boiled under a reflux condenser for 30 minutes, since it was ascertained that under these conditions asparagine²¹ splits off its amide nitrogen as ammonia quantitatively. Inasmuch, however, as it was noticed that the quantity of ammoniacal nitrogen increases with the duration of the hydrolysis, another extract was treated as described above, except that the hydrolysis was allowed to continue for 12 hours. The evaporated hydrolysate was distilled with magnesium oxide and the ammonia thus obtained titrated with standard acid. The results secured are summarized in Table III.

Table III
Proportion of Acid Amide Nitrogen in the Ungerminated Wheat Kernel

Ammoniacal nitrogen split off by hydrolysis with acid forms Acid amides Compounds other than acid amides (Hydrolyzed for 30 minutes) (Hydrolyzed for 12 Lours)

Variety of wheat	Oven- dried %	Air-dried	Total nitrogen	Water- soluble nitrogen	Oven- dried %	Air-dried %	Total nitrogen	Water- soluble nitrogen
Fultz	0.026	0.023	1.46	8.76	0.006	0.005	0.34	2.08
Marquis	.058	.052	1.91	12.33	.036	.033	1.18	7.63
Kanred	.053	.047	1.88	12.99	.017	.015	0.59	4.12
Kubanka	.052	.048	1.72	12.61	.032	.029	1.05	7.75

The numbers in Table III, each of which ordinarily represents the average of two or three individual estimations, need some explanation. When hydrolyzed for but 30 minutes the flour extract yields the total nitrogen of acid amides as ammonia, which is recorded in Cols. 2 to 5. However, when hydrolyzed for 12 hours it yields as ammonia both the nitrogen of acid amides and that of compounds other than acid amides, such as allantoin, which was shown to be present in the wheat embryo²² and is known to split off ammonia²³ when boiled with acids. it is necessary to subtract the ammoniacal nitrogen obtained on hydrolysis of the extract for 30 minutes from that secured by hydrolysis for 12 hours in order to obtain the ammoniacal nitrogen of compounds other than acid amides. It is this difference that is recorded in the last 4 columns. It will be noticed that the percentage of acid amide nitrogen in Fultz is much lower than in Marquis, Kanred and Kubanka, which show practically no difference among themselves in this respect. Similarly, the nitrogen from compounds other than acid amides (allantoin and similar substances) is lowest in Fultz, higher in Kanred and still higher in Marquis and Kubanka.

The occurrence of polypeptides or substances of a peptide character in vegetable and, generally speaking, in biological materials appears to have been variously reported by a number of investigators.

²¹ Jodidi, Kellogg and True, J. Agr. Research, 15, 398 (1918).

²² J. Landw., **52**, 322 (1904). Ref. 4.

²³ Abderhalden, "Handbuch der Biochemischen Arbeitsmethoden, Urban and Schwarzenberger, Berlin, 1910, vol. 2, p. 514.

Thus, by hydrolyzing gliadin Osborne and Clapp²⁴ succeeded in isolating a dipeptide of proline and phenylalanine. Levene and Wallace²⁵ by the action of trypsin on gelatin, obtained a polypeptide which on hydrolysis yielded proline and glycocoll while Levene and Beatty²⁶ by the action of 25% sulfuric acid on gelatin, managed to obtain peptide-like substances. By the action of pancreatin on different proteins Fischer and Abderhalden²⁷ obtained a polypeptide that was made up of all the proline and phenylalanine, and in part of other amino acids that could be obtained by hydrolysis of the proteins in question. Hart²⁸ reported that the water-soluble nitrogen of feeding stuffs is largely composed of free amino acids and peptide linkings. A few years later the occurrence of peptides in healthy and mosaic-diseased spinach²⁹ and cabbage³⁰ was reported.

A very diligent search of the literature revealed the fact that polypeptides have thus far never been reported to occur in the *ungerminated wheat kernel*.

If the aqueous flour extracts contain polypeptides, they must, when hydrolyzed long enough, yield free amino acids according to the equation,

> $NH_2RCONHR^1COOH + H_2O = NH_2RCOOH + NH_2R^1COOH$ Polypeptide Amino acids

Hence, the increase in amino acids after hydrolysis over that present before hydrolysis must correspond to the free amino groups of the peptides.

The following method was adopted in order to demonstrate the presence of polypeptides in the wheat kernel.

The preparation of the aqueous and alcoholic extracts up to the point where the alcohol is distilled was effected as outlined above. In order to remove the protein matter completely, the dry residue from the alcoholic extract was dissolved in hot water. The solution was brought to boiling, and treated successively with acetic acid, and then with freshly prepared lead hydroxide and a little lead acetate, the mixture being boiled and filtered after each treatment. The final clear filtrate was concentrated in a vacuum and made up to 100 cc. In two 20cc. portions of this the nitrogen was estimated according to the Kjeldahl method. To 50 cc. of the remaining solution hydrochloric acid was added to a concentration of 20%. This solution was boiled under a reflux condenser for 12 hours. The hydrolyzed substance was then evaporated to dryness, transferred quantitatively to a Kjeldahl flask and, in order to remove the ammonia, distilled with one31 g. of magnesium oxide previously reduced to cream with water. The magnesium oxide residue in the Kjeldahl flask was thoroughly extracted with hot water and filtered. The filtrate and washings were concentrated and made up to 100 cc., of which 2 portions of 20 cc. were analyzed by the Kieldahl method, while the remaining 50 cc. was used for formol-titration. The data secured are contained in Table IV.

Examination of Table IV, whose figures represent the average of three or four individual determinations, reveals the fact that the 4 wheat va-

²⁴ Osborne and Clapp, Am. J. Physiol., 18, 123 (1907).

²⁵ Levene and Wallace, Z. physiol. Chem., 47, 143 (1906).

²⁶ Levene and Beatty, ibid., 49, 247 (1906).

²⁷ Fischer and Abderhalden, ibid., 39, 81 (1903).

²⁸ Hart, J. Biol. Chem., 22, 477 (1915).

²⁹ Ref. 12, p. 1061.

³⁰ Jodidi, This Journal, 42, 1883 (1920).

³¹ Jodidi and Moulton, ibid., 41, 1526 (1919).

rieties investigated contain considerable proportions of peptide nitrogen, the percentages for Kanred, Fultz, Marquis, and Kubanka being, respectively, 26.86, 28.09, 32.20 and 37.76 calculated to the water-soluble nitrogen, and 3.89, 4.67, 4.98 and 5.13 calculated to the total nitrogen.

Table IV

Proportion of Peptide Nitrogen in the Ungerminated Wheat Kernel³²

Amino acid nitrogen found after hydrolysis

Amino acid nitrogen found before hydrolysis

Peptide nitrogen

Variety of wheat	Oven- dried %	Air- dried %		Water- soluble nitro- gen %	Oven- dried	Air- dried %	Total nitro- gen %	Water soluble nitro- gen	Oven- dried	Air- dried	Total nitro- gen	Water- soluble nitro- gen
Fultz	0.116	0.101	6.44	38.75	0.032	0.028	1.77	10.66	0.084	0.073	4.67	28.09
Marquis	.205	. 185	6.75	43.66	.054	.049	1.77	11.46	151	. 136	4.98	32.20
Kanred	.177	.157	6.23	43.11	.066	059	2.34	16.25	.111	.098	3.89	26.86
Kubanka	. 196	.180	6.48	47.67	.041	.037	1.35	9.91	.155	. 143	3.13	37.76

While by the method as outlined for the peptide nitrogen determination the proteins proper are quantitatively removed from the flour extracts, this may not be fully the case with the proteoses present in wheat and with the peptones whose formation during the flour extraction, in minute amounts, is very hard to prevent. It is evident that hydrolysis of these compounds, if present, just as the hydrolysis of peptides, is bound to raise the amino acid content of the flour extracts. It seemed imperative, therefore, to devise a method by which the proteoses and peptones are removed completely before hydrolysis takes place. We proceeded as follows.

The dry alcoholic extract of a definite amount of flour, prepared as already outlined, was dissolved in water and made up to 200 cc. Two portions of 10 cc. each were used for nitrogen estimation. The remaining 180 cc. was made up to 200 cc. and divided into 2 equal parts. To each of those were added 5 g. of sulfuric acid mixed with 30 cc. of a solution containing 20 g. of phosphotungstic acid and 5 g. of sulfuric acid per 100 cc. After about 24 hours the precipitates were filtered off and washed with a solution containing 2.5 g. of phosphotungstic acid and 5 g. of sulfuric acid per 100 cc. Combined filtrates and washings were freed from phosphotungstic and sulfuric acids by treatment with baryta whose excess was precipitated with carbon dioxide. The mixture was then brought to boiling and filtered. The residue on the filter was extracted with ammonia-free water. The filtrate and washings were concentrated under reduced pressure, made up to a definite volume, and the peptide nitrogen was estimated after hydrolysis with hydrochloric acid as outlined above.

By this method in which proteoses and peptones, if present, are completely precipitated by phosphotungstic acid, it was found that Kanred, Fultz, and Marquis contain respectively 27.05, 29.35 and 35.14% of peptide nitrogen as against 26.86, 28.09 and 32.20% recorded in Table IV (last column). It is true that the results obtained by the last outlined method,

³² While the results presented in this paper are based upon standard methods, the complexity of the substances contained in plant materials renders it extremely difficult, if at all possible, to effect a strictly quantitative separation of the various compounds. This should be borne in mind when examining the data in Tables II to IV.

the details of which will be given in a subsequent paper, are not strictly comparable with those of Table IV for the reason that phosphotungstic acid precipitates, in addition to proteoses and peptones, also diamino acids, ammonia, bases like choline, betaine, etc. Broadly speaking, however, the results obtained by the last method fully corroborate the outstanding fact presented in Table IV that the wheat varieties in question contain in their ungerminated kernel considerable proportions of peptide nitrogen. The presence of peptides in the wheat kernel may have considerable physiological significance, such as in protein synthesis and more generally in nitrogen metabolism, because of the fact that they form a necessary link between the amino acids on the one hand and the proteins on the other.

Summary

The results thus far obtained permit drawing the following conclusions.

- 1. The wheat varieties investigated contain peptides in their ungerminated kernels, the percentages of peptide nitrogen for Kanred, Fultz, Marquis, and Kubanka being, respectively, 26.86, 28.09, 32.20 and 37.76, on the basis of the water-soluble nitrogen, and 3.89, 4.67, 4.98 and 5.13, calculated to the total nitrogen.
- 2. The wheat varieties under consideration contain free amino acids in their ungerminated kernels, the proportions (in round figures) for Kubanka, Fultz, Marquis, and Kanred being, respectively, 10, 11, 11 and 16% of amino acid nitrogen, calculated to the water-soluble nitrogen, and 1.4, 1.8, 1.8 and 2.3%, calculated to the total nitrogen.
- 3. The proportions of acid amide nitrogen in the ungerminated kernel of the varieties Fultz, Marquis, Kubanka and Kanred are, respectively, 8.76, 12.33, 12.61 and 12.99%, calculated to the water-soluble nitrogen, and 1.46, 1.91, 1.72 and 1.88% calculated to the total nitrogen.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE CATALYTIC REDUCTION OF NITRO COMPOUNDS. II. GAMMA-NITRO KETONES

By E. P. Kohler and N. L. Drake Received June 14, 1923

The first step in the reduction of nitro compounds, the transition from nitro to nitroso compounds or, in the case of primary aliphatic nitro compounds, to oximes is as yet a complete mystery. Since γ -nitro ketones on hydrogenation would form substances in which active hydrogen and a carbonyl group are in a relation that is favorable for intramolecular condensation, it seemed possible that they might serve better than simpler nitroparaffins for permitting an insight into this process. With this end in view we have reduced the following 3 nitro ketones.

The results are disappointing, for while the reduction products undergo internal condensation as expected, the condensation products are themselves so easily reduced that it is impossible either to confine the action to a single step or to deduce the successive steps from the products finally obtained. The final result, moreover, depends to such a degree upon factors that cannot be controlled, that both the nature of the products and their relative amounts vary in reductions which are carried out as nearly as possible under the same conditions.

Thus in an experiment with the nitro ketone II in which the operation was interrupted when approximately 2 molecular equivalents of hydrogen per equivalent of ketone had been absorbed, the solution contained unchanged nitro ketone, the amino ketone IV, an hydroxy pyrroline V or VI, and the pyrrolidine VII.

The 3 reduction products, the only ones obtained by reducing this nitro ketone under a variety of different conditions, are here formed side by side long before all of the nitro compounds have disappeared from the solution, and neither the nature of the products nor the rate at which hydrogen is consumed gives any clue as to the stage at which condensation takes place.

The amino ketone IV is the only open chained reduction product that we obtained from any of these nitro ketones. It is also the only γ -amino ketone that is known, all earlier attempts to prepare this type of compound having failed, owing to the ease with which such compounds undergo internal condensation.1 While it readily undergoes this condensation, it is stable in neutral and weakly alkaline solutions. It is unlikely, therefore, that the pyrrolidine derivative VII is formed by way of the amino ketone.

The hydroxy pyrroline also represents a new type of compound. It was isolated with such difficulty and in such small quantities that its

¹ Hielscher, Ber., 31, 278 (1898). Gabriel, ibid., 42, 1242 (1909). Gabriel and Colman, ibid., 42, 1248 (1909).

structure could not be established with certainty; the only facts available are its composition and its ability to form a benzoyl derivative. Its indifference to permanganate in acetone is hard to reconcile with either formula. Since it is always present in the solutions after all absorption of hydrogen has ceased, it cannot be the source for the pyrrolidine derivative. The 3 reduction products, amino ketone, pyrroline, and pyrrolidine, must therefore be reached by separate paths.

The relative amounts of the 3 reduction products vary greatly with the nature of the nitro ketone. The 2 phenyl ketones give but small quantities of pyrrolidine derivatives, but in the case of the methyl ketone this is the principal product. Since the reduction takes place very readily and it is easy to isolate the product without allowing it to come in contact with air, this is at present, doubtless, the best method for getting pyrrolidine derivatives with groups in the 2,5 positions. The yield from the nitro ketone I was 86.5%.

Experimental Part

The reductions were carried out by shaking suspensions or solutions of the nitro ketones in methyl alcohol with hydrogen in the presence of 0.5 g. of Loew's platinum black. As the nitro ketones are only moderately soluble, solutions were used only in attempts to get earlier stages of reduction. The rate at which hydrogen was absorbed was measured but it had little significance beyond indicating whether or not the reduction was proceeding normally. When suspensions were used, the rate of absorption usually remained constant until all of the solid had disappeared, then slowly fell off, and finally stopped when approximately 4 molecules of hydrogen had been absorbed for 1 of the ketones. In the few cases in which a sharper break in the absorption curve was observed, the corresponding quantities of hydrogen did not represent any definite stages of reduction.

During the reduction the catalyst changed into a more compact form, hence was easily removed by filtration. If the reduction to the pyrrolidine derivative was complete, the clear filtrate remained colorless both when allowed to remain in contact with air, and when treated with acid. But if the operation was interrupted before the reduction was completed, the colorless liquid soon became pink and the color gradually deepened to dark red or purple.

I. γ -Nitro- β -phenyl Pentanone

Preparation.—The nitro ketone was made by adding nitromethane to benzalacetone. The addition takes place readily, but the yield is not nearly so satisfactory as that obtained with benzalacetophenone, and even under the most favorable conditions half of the material goes into oily products. The best procedure was as follows.

A paste of sodium nitromethane was made by adding gradually and with constant stirring 15 g. of nitromethane to a well-cooled solution of 5 g. of sodium in 50 cc. of dry methyl alcohol. This was added rapidly to a solution of 25 g. of benzalacetone in 50 cc. of dry methyl alcohol that had previously been heated to near the boiling point. The mixture was kept at this temperature, and shaken vigorously to ensure as rapid addition as possible. As soon as all the solid had disappeared the clear, orange-colored solution was cooled in an ice-and-salt mixture and then acidified very slowly with 20 g. of glacial acetic acid. The nitro ketone slowly separated as a pasty solid. After standing for an hour the crystal mass was filtered, pressed on a suction funnel, washed first with a little alcohol and then very thoroughly with water, pressed as dry as possible, and dissolved in chloroform. The water layer was separated, the chloroform solution dried with calcium chloride, and freed from chloroform by distillation. The residue thus obtained was recrystallized from methyl alcohol from which it separated in lustrous needles. The substance is moderately soluble in cold ether and methyl alcohol; m. p., 99–100°; yield, 48%.

Analysis. Calc. for C₁₁H₁₃O₃N: C, 63.8; H, 6.3. Found: C, 63.7; H, 6.4.

REDUCTION.—A suspension of 40 g. of the nitro ketone in 200 cc. of methyl alcohol was shaken with hydrogen and 0.5 g. of platinum black until absorption ceased. The platinum was then removed from the solution by filtration, the methyl alcohol distilled, and the residue subjected to vacuum distillation. This gave, along with a small quantity of low-boiling product and a tarry residue, 27 g. of a colorless oil which on redistillation boiled at 112° (10 mm.). As this proved to be extremely hygroscopic it was distilled from sodium in preparation for analysis.

Analysis. Calc. for C11H15N: C, 82.0; H, 9.3. Found: C, 81.7; H, 9.4.

2-Methyl-4-phenyl-pyrrolidine, $C_6H_5CH-CH_2-CHCH_3$.—This is a colorless CH_2-NH

liquid which can be kept unchanged in sealed tubes, but which gradually turns yellow when exposed to the air. It is most easily identified by its solid benzoyl derivative.

chloride was gradually added in excess to an ethereal solution of the pyrrolidine derivative which was then shaken with 10% potassium hydroxide until the odor of the chloride had disappeared. The ethereal solution was dried over calcium chloride, the ether removed, and the residue distilled under diminished pressure. It distilled without decomposition at 260–270°, and the colorless distillate solidified in large, colorless tablets melting at 79–80°. When the substance was recrystallized from a mixture of ether and petroleum ether the melting point became constant at 82–83°. The substance crystal-

lizes in large prisms. It is readily soluble in ether or alcohol, sparingly in ligroin.

Analysis. Calc. for C₁₈H₁₉ON: C, 81.5; H, 7.2. Found: C, 82.0; H, 7.2.

1,2-Dimethyl-4-phenyl-pyrrolidine Hydrobromide, C₆H₅CH—CH₂—CHCH₃

CH₂——NCH₃HBr.—

Methylphenyl-pyrrolidine reacts very energetically with methyl iodide, but it is difficult to isolate a pure product even when the reaction is moderated by diluting the reagents with dry ether. It is better, therefore, to methylate with dimethyl sulfate. For this purpose 8 g. of dimethyl sulfate was gradually added to 5 g. of the base suspended in 70 cc. of 10% potassium hydroxide solution which was cooled in ice and salt. The mixture was shaken until all of the sulfate was hydrolyzed, then extracted with ether. The ethereal solution was dried with solid potassium hydroxide and finally with metallic sodium. From the resulting solution dry hydrogen bromide precipitated the hydro-

bromide of the methylated compound in fine, colorless needles. After recrystallization from methyl alcohol ether these melted at 144-146°, probably with decomposition.

Analysis. Calc. for C12H17NHBr: C, 56.3; H, 7.0. Found C, 56.6; H, 7.0.

II. β -(3,4-Methylene-dioxy-phenyl)- γ -nitro-butyrophenone

Preparation and Properties.—The method of preparation was the same as that used in the case of γ -nitro- β -phenyl pentanone, but the yield was much better; 68 g. of piperonal acetophenone condensed with 30 g. of nitro methane gave 61 g. of the nitro ketone.

The substance was purified by recrystallization from methyl alcohol. It separated in fine needles that melted at $95-96^{\circ}$.

Analysis. Calc. for C₁₇H₁₅O₅N: C, 65.2; H, 4.8. Found; C, 65.0; H, 5.1.

REDUCTION.—A solution of 31.3 g. of the nitro ketone in 200 cc. of methyl alcohol was reduced in the presence of 0.5 g. of platinum. The solution began to absorb hydrogen at a rate of about 2.3 cc. a minute. This rate was maintained with little change until somewhat more than the quantity of hydrogen had been absorbed which was calculated for reducing the nitro to the amino group. It then dropped sharply to nearly a third of this value and remained constant at the new level until absorption ceased.

A colorless solid separated from the solution during the reduction and remained mixed with the catalyst when the operation was stopped. This was filtered off, washed with ether, and dissolved in boiling dry methyl alcohol. It crystallized in colorless needles, but the melting point was less sharp than it had been before solution. It was, therefore, recrystallized from dry ether and ligroin before analysis.

Analysis. Calc. for C₁₇H₁₇O₃N: C, 72.1; H, 6.0. Found: C, 72.4; H, 6.0.

 β -(3,4-Methylene-dioxy-phenyl)- γ -amino-butyrophenone, IV.—The amine is readily soluble in chloroform and acetone, moderately soluble in methyl alcohol and in ether, slightly soluble in ligroin. It crystallizes in colorless needles or plates and melts at 129–130°. When it is perfectly pure and dry it is stable; but in solution and when moist it changes more or less rapidly into gummy, discolored condensation products. It appeared to form a hydrochloride, but this was not adapted either for purification or identification.

2-Phenyl-4-(3,4-methylene-dioxy-phenyl)phenyl Sulfone,

CH₂-N—SO₂C₆H₅.—When the amine is treated with benzene sulfone chloride and alkali it undergoes both acylation and condensation. The product is a sparingly soluble sulfone which crystallizes well and serves to distinguish between the amine and all other substances except the corresponding pyrrolidine. The substance is very sparingly soluble in ether, somewhat more readily soluble in methyl alcohol, readily soluble in chloroform. It was purified by recrystallization from chloroform-petroleum ether. It crystallizes in minute plates, begins to turn brown at 220°, and melts with decomposition at 225–227°.

Analysis. Calc. for C23H19O4NS: C, 68.1; H, 4.7. Found: C, 68.6; H, 4.9.

PARTIAL REDUCTION.—Since the preceding experiment showed a fairly sharp drop in the rate of reduction after 2 molecular equivalents of hydrogen had been absorbed, we repeated it as nearly as possible under the same conditions, but interrupted the operation when the solution which contained 31.3 g. of ketone had absorbed 4.97 l. of hydrogen. The liquid contained no solid other than platinum. This was removed and the

filtrate concentrated and set aside. It deposited $7.0~\rm g$. of unchanged nitro ketone which was identified by a mixed melting point. After further concentration it deposited $3.3~\rm g$. of a mixture of nitro ketone and amine, and later $4.5~\rm g$. of a new product that melted at $144-145~\rm c$. Finally, when all the alcohol was removed, there remained a gummy residue that could not be induced to crystallize.

1-Hydroxy-2-phenyl-4-(3,4-methylene-dioxy-phenyl)-pyrroline, VI.—The solid that melted at 144-145° was purified by recrystallization from methyl alcohol or ether. It crystallizes in colorless needles, is moderately soluble in alcohol, ether or benzene, is not changed by contact with air, and does not reduce permanganate in acetone.

Analyses. Calc. for C₁₇H₁₅O₂N: C, 72.6; H, 5.3. Found: C, 72.5, 72.4; H, 5.6, 5.6.

2-Phenyl-4(3,4-methylene-dioxy-phenyl)pyrrolidine Hydrochloride, VII.—The gummy mass left after all of the alcohol had been removed turned dark red or purple on treatment with hydrochloric acid. On cautious dilution with a mixture of methyl alcoholic hydrogen chloride and ether it deposited a solid that crystallizes from alcohol and ether in beautiful, long, thin, white needles. The color of the solution was doubtless due to the presence of the amino ketone, because the solutions of the pyrrolidine hydrochloride in methyl alcohol and in ether are colorless, and remain so when left in contact with air. The salt melts with decomposition at about 208°.

Analysis. Calc. for C₁₇H₁₇O₂NHC1: C, 67.2; H, 5.9. Found: C, 67.2; H, 5.8.

III. β -Phenyl- γ -nitro-butyrophenone

The nitro ketone III gave only oily products that could not be distilled under diminished pressure. By indirect methods it was possible to prove that these oils contained an hydroxy pyrroline, which was isolated as benzoate VIII or IX, and the pyrrolidine X which was isolated as hydrochloride and oxalate.

2,4-Diphenyl-pyrrolyl Benzoate, VIII or IX.—A small quantity of the oil, left after distillation of the methyl alcohol in which the nitro ketone had been reduced, was mixed with 5 times its weight of benzoyl chloride and an excess of 10% potassium hydroxide. The mixture immediately turned to a deep purple. It was shaken until the odor of benzoyl chloride had disappeared, then diluted with water and separated. The oil was washed with water and dissolved in methyl alcohol. This solution deposited a solid which was recrystallized from methyl alcohol. It separated in colorless needles; m. p., 179–180°.

Analysis. Calc. for C23H19O2N: C, 80.9; H, 5.6. Found: C, 80.5; H, 5.4.

2,4-Diphenyl-pyrrolidine Hydrochloride.—A methyl alcoholic solution of the oil obtained by reducing phenylnitro-butyrophenone was saturated with dry hydrogen chloride, then cautiously diluted with dry ether until a slight cloudiness appeared, and set aside. It deposited thin, colorless needles which were recrystallized from dry methyl alcohol and ether; m. p., 171–172°.

Analysis. Calc. for C₁₆H₁₇NCl: C, 74.0; H, 6.9. Found: C, 73.9; H, 6.9.

Di(2,4-diphenyl)pyrrolidine Oxalate.—A solution of 5.4 g. of the nitro ketone in 50 cc. of methyl alcohol was reduced in the presence of 0.9 g. of oxalic acid and 0.5 g. of platinum black. A colorless solid began to separate long before all of the nitro compound had disappeared from the solution. As it was impossible to dissolve the sparingly

soluble salt without decomposing it, the mixture of salt and platinum was thoroughly dried and analyzed, the amount of platinum in the sample being determined by weighing the boat after the analysis.

Analysis. Calc. for C₃₄H₂₅O₄N₂: C, 76.1; H, 6.7. Found: C, 75.7; H, 6.8.

Both the pure hydrochloride and the pure oxalate were decomposed with alkali in the hope of getting a solid pyrrolidine, but the product in each case was a colorless oil.

Summary

- 1. When γ -nitro ketones are reduced with hydrogen in the presence of Loew's platinum black there is a succession of reduction and condensation reactions that overlap to such a degree that the rate at which the hydrogen is absorbed is represented by a smooth curve.
- 2. The principal reduction products are the amino ketone, hydroxypyrroline and pyrrolidine, corresponding to the nitro ketone that is reduced.
- 3. These products do not represent successive stages in the reduction; they are formed, simultaneously, along different routes.

Cambridge 38, Massachusetts

[Contribution from the Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, and the Laboratory of Physiological Chemistry, Tulane University School of Medicine]

DETERMINATION OF FORMALDEHYDE IN PRESENCE OF SUBSTANCES FOUND IN FORMALIN

By P. Borgstrom Received June 15, 1923

The object of this paper is to present the results of a study of certain methods for the determination of formaldehyde in the presence of some of the organic substances that may be present in a formalin solution. The substances whose effect will be noted are methyl alcohol, ethyl alcohol, sodium formate, acetone and methylal.

The methods chosen are (1) iodimetric, (2) "alkali-peroxide" and (3) neutral sulfite. These methods have been studied in previous work, and as the procedure used in this work is the same no detailed explanation of the procedure will be given.

The paraformaldehyde used is the same as in previous work, and gave by the Liebig combustion method 96.8% of formaldehyde and 3.2% of water. Sodium formate was

¹ The determination of formaldehyde, methyl alcohol, and sodium formate in the same solution was attempted by the oxidation with permanganate and the absorption of the carbon dioxide produced. The method used is that suggested by Messinger [Ber., 21, 2910 (1888)]. By this method the purity of the methyl alcohol was determined to be 95.35% and the sodium formate 100%; 0.2466 g. of paraformaldehyde and 0.7510 g. of sodium formate produced 0.8284 g. of carbon dioxide; calc., 0.8352 g.; 0.1170 g. of paraformaldehyde, 0.2722 g. of sodium formate and 0.2270 g. of methyl alcohol produced 0.6448 g. of carbon dioxide; calc., 0.6397 g.

² Borgstrom and Horsch, This Journal, 45, 1493 (1923).

used as a source of formate ion due to the ease of purification. The methyl alcohol was acetone-free but no attempt was made to have it absolute. The ethyl alcohol was absolute but no special purification was attempted to free it from traces of aldehydes. The acetone used was from the bisulfite compound. The methylal was used as purchased. From the odor of iodoform given off during use in the iodimetric method it may have had a trace of either acetone or ethyl alcohol and because of this no extensive investigation was made with it.

The substance whose effect was to be studied was added to the weighed paraformaldehyde.³ With liquids, especially with methyl alcohol and methylal, the materials to be added were sealed in small tubes of known weight. Most of the work was done by weight except in a few cases in which a micro-buret calibrated to 0.02 cc. was used.

Iodimetric Method.—No difference could be detected in the ratio of iodine to thiosulfate due to the presence of sodium formate in amounts ranging from 0.003 to 0.044 molecular equivalent.

The average net consumption of $0.0803\ N$ iodine was $0.140\ {\rm cc.}$ per g. of methyl alcohol. Using this value, one mole of methyl alcohol reacts with an iodine equivalent of $0.0066\ {\rm g.}$ (or $0.00022\ {\rm mole}$) of formaldehyde. This means that when both are present in the same concentration the determination will be 0.022% high.⁴

To show the actual effect of sodium formate and methyl alcohol nine determinations with a ratio of moles of HCOONa to moles of HCHO ranging from 1.24 to 4.26 gave an average value of 96.72% with an average deviation of 0.28. Seven determinations with the ratio of moles of CH₃OH to moles of HCHO ranging from 4.9 to 46.1 gave an average value of 97.0% with an average deviation of 0.18. Twelve determinations with a ratio of moles of HCOONa to moles of HCHO of 2.72, 8.84, 3.64, 5.65, 1.07, 3.55, 2.73, 4.78, 4.16, 4.19, 3.69 and 2.82 and the corresponding ratio of moles of CH₃OH to moles of HCHO of 20.6, 11.4, 14.1, 21.7, 16.2, 11.1, 7.0, 13.9, 31.7, 11.2, 7.8, 23.0, gave the percentage of formaldehyde as 96.90, 97.52, 96.47, 96.79, 96.23, 96.80, 97.19, 97.00, 97.39, 96.83, 96.86, and 97.25, respectively, with an average value of 96.93 and an average deviation of 0.28. This shows that the concentration of methyl alcohol and sodium

- ³ A paper by F. Mach and R. Herrmann has just appeared [Z. anal. Chem., 62, 104 (1923); C. A., 17, 945 (1923)] on "A Comparison of the Most Useful Methods for the Determination of the Formaldehyde Content of Formalin Solutions." The conclusions drawn by them differ somewhat from the results found in the present work and may be due to the fact that they used a formalin solution, while in this work paraformaldehyde was used as a standard.
- ⁴ L. F. Goodwin [This Journal, **42**, 44 (1920)] has found that "0.5 cc. methyl alcohol causes an error of nearly 0.5 cc. in the amount of 0.1 N iodine solution used." This value is higher than that found by the author and may be explained by the difference in quality of the methyl alcohol. If the alcohol be very carefully purified and used when fresh it probably will have no reaction or but very slight with alkaline iodine solutions.

formate in an ordinary formalin solution has no effect on the titration by the iodimetric method.

As both acetone⁵ and ethyl alcohol⁶ react rapidly with an alkaline iodine solution, error in the results would be dependent upon the concentration of these present and, therefore, no further work was done in connection with this method.

With methylal there was a reaction with the alkaline-iodine solution, and a strong odor of iodoform developed and in some cases even a precipitate. This may be due to either ethyl alcohol or acetone. The consumption of iodine $(0.0759\ N)$ per gram of the methylal was $11.07\ cc.$ as an average for 5 trials. Because of this no direct determinations were made with methylal present.

Hydrogen Peroxide Method.—The previous work was repeated; 7 determinations gave an average value of 96.86% with an average deviation of 0.23%. An attempt was made to use cresol red (o-cresol-sulfon-phthalein) as an indicator in place of litmus but the results were 98.71 and 98.01%, showing that under this condition this indicator was not satisfactory. When litmus was used as an indicator and the solution allowed to stand for an hour as recommended by Mach and Herrmann³ the purity found was 97.34% (5 determinations) with an average deviation of 0.20%. When cresol red was used under the same conditions the average value was 96.92% (7 determinations) with an average deviation of 0.21%.

When 5 cc. of methyl alcohol (calculated to be about 3.93 g.) was heated for 5 minutes, the net consumption of 1.0 N sodium hydroxide solution as calculated for per mole of methyl alcohol was 0.250 cc. or a negligible error. When 5 cc. was heated for 10 minutes the calculated consumption per mole was 2.304 cc. of N alkali. Mole for mole the error would not be over 0.25% even if the methyl alcohol were heated for 10 minutes.

When 1.9883, 1.4544, 1.1735 and 2.2280 g. of ethyl alcohol were heated with "alkaline peroxide" the net consumption of N alkali per mole of alcohol was 0.16, 1.53, 4.48 and 7.92 cc. for time of heating 5.5, 6, 8.5 and 27.5 minutes, respectively. The error is very small when the solution is molar, in formaldehyde and ethyl alcohol, and time of heating 5 minutes but with 8 minutes' heating the error is about 0.5%.

Three trials were made with methylal using 0.2379, 0.1799 and 0.2789 g. heated for 5 minutes and then cooled rapidly. The ratio of the acid and alkali used in these experiments was 1.1672, with an average deviation of 0.0005 in 8 trials. The trials with methylal showed a difference from this mean of 0.0017, 0.0003 and 0.0011 or an average of 0.0010. This is twice the error found without methylal. There is a trace of acetone or ethyl

⁵ Messinger, Ber., 21, 3366 (1888).

⁶ Luben, Ann. Spl., 7, 218, 377 (1870).

alcohol in the methylal (as shown by the iodimetric method) and this probably accounts for the difference. The actual difference as found is -0.04, +0.01, -0.02 cc. for the three runs. In one trial in which 0.4137 g. of methylal was allowed to stand for 45 minutes and gradually cool after heating for 5 minutes, the result was a net consumption of 0.11 cc. of N alkali; if both methylal and formaldehyde were molar the results on this account would be 2% high.

The action of alkaline peroxide on acetone is greater than on methyl or ethyl alcohol. When the mixture was heated for 5 minutes and then rapidly cooled the consumption of N alkali was 0.10, 0.05 and 0.15 cc. for 0.270, 0.320 and 0.410 cc. of acetone. Using the density of 0.78637 for acetone one mole reacted, therefore, with 27.32, 11.53 and 26.93 cc. of N alkali, respectively, giving thus an error of 2.7, 1.15 and 2.7%, respectively, if the concentration of each is molar.

Table I shows the actual effect of these substances on the determination of formaldehyde by the peroxide method. No attempt was made to cool

Table I

Effect of Added Substances on the Determination of Formaldehyde in Paraformaldehyde by the Peronide Method

Paraformal-	2020	IIIDIIII DI	1112 1 4101112			
dehyde	Moles HCOONa				~ ~~~	
G.	Moles HCHO	Moles HCHO	Moles HCHO	Moles HCHO		
0.4104	1.145	• •	• •		96.34	
.4212	1.12		• •		96.77	
.3922	1.85			1 *1 * ·	96.69	
. 3639	1.31	2.59			97.22	
4003	0.64	1.98			97.65	
. 3525	1.19	3.79			97.73	
.3742	1.65	5.14			97.59	
. 4258	1.11	3.18			96.94	
.3917		0.280			97.10	
. 5754		. 304			96.75	
.5989		.261			96.56	
.4589		.390			96.50	
.3460	0.71		2.73		97.14	
4169		•	2.65.		97.21	
.4271	, .,		1.51		96.99	
.3106			1.11		97.20	
.3807		* *	2.88		96.82	
.4183			2.38		97.17	
.4562		0.369	.279		97.33	
. 5390		.162	.104		97.31	
.4710		.170	.103		96.70	
.4546				0.161	97.34	
.4847		1.1		.140	97.46	
.4517		1		.098	97.23	
.2981				.115	97.42	
.2839				.197	97.69	
			00 (000)			

⁷ Krug and Elroy, Z. anal. Chem., 32, 106 (1893).

Runs 5, 6 and 7, while 8 was placed in water at about 20° for cooling. Runs 22 and 26, inclusive, show the effect of acetone. Evidently, if present in traces acetone should not have an effect when this method is used. Omitting Runs 5, 6 and 7, and 22 to 26, inclusive, the average value obtained was 96.94% with an average deviation of 0.20%, or about 0.1% higher than that found in the absence of these materials.

Neutral Sulfite Method.—No color change was noted on the addition of 1.5 g. of anhydrous sodium formate to 25 cc. of 4 N sulfite solution neutralized to rosolic acid by $0.498\ N$ sulfuric acid.

In 3 experiments the average alkalinity produced on the addition of 5 cc. of methyl alcohol to 25 cc. of neutralized sulfite solution was 0.41 cc. of 0.498 N sulfuric acid, using rosolic acid as an indicator. Assuming 5 cc. of methyl alcohol to be about 0.12 mole, the same amount of formaldehyde would require 240 cc. of 0.498 N acid for the neutralization of the base liberated by the reaction. This shows that for equal concentrations methyl alcohol causes an error of 0.16% when no correction is made for the effect of dilution.

The values given in Table II show that methylal, ethyl alcohol and methyl alcohol have no appreciable effect in the determinations by the neutral sulfite method.

Table II Determination of Formaldehyde in Paraformaldehyde 4N in Sodium Sulfite Solution, $1.169\ N$ in Sulfuric Acid, Using Rosolic Acid as Indicator

202011011, 1	.100 11 111 0001	accenter, com	TODOUTE TICLD	V2 THOTCHTON
Paraformaldehyde G.	Ethyl alcohol G.	Methyl alcohol G.	Methylal G.	CH ₂ O found, %
0.4787		0.2255		96.90
.3682	0.1457	.0780		96.85
.4258	.1422	.1555		96.92
.3155	.1500	.2333		96.80
. 4488	.1104	.2178		97.02
.3563	.1419			96.74
.4357	.1143			96.97
4385	.1498			96.99
. 5551			0.1579	96.83
.3216			. 1210	96.61
				Av. 96.86
			Av.	dev., 0.10

Acetone and neutral sulfite react, liberating alkali just as formaldehyde does. Assuming the density of acetone to be 0.8, the amount of base liberated per mole of acetone was 407.5, 410.0 and 408.0 cc. as determined by neutralization with N sulfuric acid, working with samples of 0.235, 0.310 and 0.135 cc., respectively. This substance, then, would cause an error of 40% if the concentration of formaldehyde and acetone were the same.

Paraformaldehyde in the presence of acetone, as determined by this method, gradually decreased in purity with increased time of contact

before neutralization of the alkali liberated. With the addition of 0.060 cc. of acetone to samples of paraformaldehyde of 0.45 to 0.52 g. the purity determined was 97.66, 97.03, 96.27, 96.00 and 93.70% with time intervals of 5, 10, 15, 20 and 30 minutes, respectively. When 0.4466, 0.5283 and 0.5194 g. were mixed with 0.250, 0.235, and 0.240 cc. of acetone, respectively, the purity determined was 101.34, 95.23 and 94.45% with time intervals of 5, 10 and 15 minutes, respectively.

These data show that the determinations when made within 5 minutes' time may be high but not additive. The larger the amount of acetone, the greater will be the error. The cause of the change may be due to (1) the addition of sodium sulfite to the acetone and resultant liberation of sodium hydroxide; (2) the condensation of acetone and formaldehyde under the influence of the base present, thus freeing 2 molecules of sodium sulfite; or (3) the reaction of formaldehyde with the base, forming sodium formate and methyl alcohol. The first cause would be responsible for the first increase, and the second and third causes would tend to lower the values with time, as found. No attempt was made to determine the actual cause of this variation.

Summary

- 1. The iodimetric method can be used for the determination of formaldehyde in the presence of methyl alcohol and formic acid. Methylal, if pure, should have no effect. When acetone and ethyl alcohol are present this method cannot be used.
- 2. The peroxide method as outlined can be used for the determination of formaldehyde in the presence of methyl alcohol, ethyl alcohol, formic acid and methylal. When acetone is present in equal concentrations, the determination will be about 2% high.
- 3. The neutral sulfite method can be used for the determination of formaldehyde in the presence of methyl alcohol, ethyl alcohol, formic acid and methylal. Acetone introduces an error that cannot be readily corrected.

NEW ORLEANS, LOUISIANA

[Contribution from the University of Toronto]

SOME PREPARATIONS FROM MALEIC AND FUMARIC ACIDS

By Harold G. Oddy Received June 16, 1923

Pechman¹ and Gabriel and Coleman² have prepared β -benzoyl-acrylic acid from maleic anhydride, benzene and aluminum chloride, and Pechman and Kosniewski and Marchlewski³ prepared β -toluyl-acrylic acid from maleic anhydride, toluene and aluminum chloride. This work has been repeated and the conditions for better yields determined. In the preparation of β -benzoyl-acrylic acid a yield of 95% (crude) was obtained by using 3 g. of maleic anhydride, 25 cc. of benzene, and 9 g. of aluminum chloride. This was kept cool for 20 minutes and then heated to 60° for 1.5 hours. Longer heating reduces the yield. In the preparation of β -toluyl-acrylic acid the same method gave a yield of 77%. Naphthalene, anthracene and diphenyl have been used in this experiment, giving the corresponding unsaturated keto acids, and various addition compounds of these acids have been prepared.

Rubidge and Qua's⁴ method of preparing diphenylphthalide from phthalic anhydride, benzene and aluminum chloride by using an acid anhydride on the intermediate compound has been shown to have quite general application. If maleic anhydride were substituted for phthalic anhydride in the reaction the product should be diphenyl-croton lactone but although the conditions were varied considerably the results of an attempt to effect this reaction were negative.

Since Pechmann⁵ prepared diphenylphthalide from the mixed anhydride of benzoyl-benzoic acid and acetic acid, the anhydride of β -benzoylacrylic acid and acetic acid, m. p. 113–114°, was prepared and treated with benzene and aluminum chloride but no diphenyl-croton lactone was obtained.

Fumaryl chloride, benzene and aluminum chloride have been used to prepare dibenzoyl-ethylene and instead of benzene, other hydrocarbons such as toluene, *m*-xylene and diphenyl have been used and the corresponding 1,4-diketones obtained. Since this work was done, Conant and Lutz⁶ have described the preparation of 1,4-diketones by this method using benzene, toluene, chlorobenzene and mesitylene. Paal and Schulze⁷ had prepared dibenzoyl-ethylene (*trans*) from dibenzovl-malic acid and

- ¹ Pechman, Ber., 15, 885 (1882).
- ² Gabriel and Coleman, ibid., 32, 393 (1889).
- ³ Kosniewski and Marchlewski, Chem. Centr., (2) 77, 1190 (1906).
- 4 Rubidge and Qua, This Journal, 36, 732 (1914).
- ⁵ Pechmann, Ber., 14, 1865 (1881).
- 6 Conant and Lutz, This Journal, 45, 1303 (1923).
- ⁷ Paal and Schulze, Ber., 33, 3795 (1900).

changed it to the *cis* form by exposure to sunlight. The author found that ditoluyl-ethylene (*trans*) and di-2,4-xylyl-ethylene (*trans*) prepared from fumaryl chloride were changed, on exposure to sunlight, to the colorless *cis* form. Conant and Lutz also changed their *trans* 1,4-diketones to the *cis* forms by this method but my results in the case of ditoluyl-ethylene do not quite agree with theirs.

Paal and Schulze noted that the bromine addition compounds of the trans and cis forms of dibenzoyl-ethylene were identical. The author found this to be true also for the bromine addition compounds of di-p-toluyl-ethylene and di-2,4-xylyl-ethylene.

The melting points given in this paper were taken with a mercury thermometer which was calibrated by Professor J. B. Ferguson against a standard platinum-platinumrhodium thermocouple by means of a precision potentiometer.

Experimental Part

Identification of β -p-Toluyl-acrylic Acid.—One g. of the toluyl-acrylic acid was boiled with 10% sodium hydroxide solution for a few minutes; the methyltolyl ketone separated as an oil. This oil was oxidized in a cold alkaline solution of potassium ferricyanide, giving p-toluic acid. Previous experimenters had assumed that this acid was the para derivative.

Methyl β -p-Toluyl-acrylate.—Six g. of the toluyl-acrylic acid was dissolved in methyl alcohol and the solution saturated with hydrogen chloride. The oil remaining on the evaporation of the methyl alcohol was dried and most of it distilled at 240–245° under 115 mm. pressure. After recrystallization from acetic acid it formed long, colorless crystals, m. p., 45.5–46° and was readily soluble in ether, chloroform, benzene or ethyl alcohol.

 β -p-Toluyl- α -chloropropionic Acid.—One g. of the toluyl-acrylic acid was allowed to stand with 25 cc. of concd. hydrochloric acid in a closed flask for 60 hours. The product, which was colorless, was washed with water, dried and freed from the original acid by warming it with a small amount of toluene. It was then recrystallized from a large volume of toluene; m. p., 144–144.5°. It is quite soluble in acetone or ethyl alcohol and less so in ether or chloroform. Since, in the analogous compound, β -benzoyl-chloropropionic acid, prepared by Bougault, β the chlorine was in the α -position, this compound is β -p-toluyl- α -chloropropionic acid.

Analysis. Cale. for C11H11O3C1: Cl, 15.65. Found: 15.45.

 β -p-Toluyl- β , α -dibromopropionic Acid.—In cold acetic acid solution the toluyl-acrylic acid immediately reacted with bromine. Very pure material was obtained by recrystallizing the product from 75% methyl alcohol. It is soluble in chloroform, benzene, acetone or ethyl alcohol.

Analysis. Calc. for C11H10O3Br2: Br, 45.67. Found: 45.25.

 β , β -Naphthoyl-acrylic Acid.—Five g. of maleic anhydride and 7 g. of naphthalene were dissolved in 35 cc. of benzene, and 15 g. of aluminum chloride was slowly added. After 30 minutes the flask was warmed to $60-70^{\circ}$ for 4 hours. After decomposition of the intermediate compound with hydrochloric acid and removal of the benzene and excess naphthalene by distillation with steam the crude product was dissolved in sodium hydroxide solution and the solution gradually acidified, the first precipitate being re-

⁸ Bougault, Ann. chim. phys., [8] 15, 499 (1909).

jected. A small amount of benzoyl-acrylic acid was removed by washing the crystals with benzene and the material was further purified by recrystallizing it from a large volume of 10% hydrochloric acid; it seemed to be principally one product. By making the methyl ester of this material and hydrolyzing the ester, a pure acid, m. p., 189–190°, was obtained. It is easily soluble in acetone, ether, acetic acid, alcohol or chloroform and slightly soluble in benzene. In one preparation a small amount of a second product, m. p., 158–159°, was obtained which seemed to be more soluble in benzene, and the methyl ester was an oil. The acid, m. p., 189–190°, did not react with bromine in cold acetic acid solution, and in hot acetic acid hydrogen bromide was evolved.

Analysis of silver salt. Calc. for C14H9O3Ag: Ag, 32.5. Found: 31.9.

Identification of the Acid Melting at 189–190°.—One g. of this acid was dissolved in acetic acid and 6 g. of sodium dichromate added. The flask was kept on the water-bath for 6 hours and after it had then cooled the contents were diluted with thrice their volume of water. A brown precipitate formed that on sublimation gave β -naphthoic acid. The acid is, therefore, β , β -naphthoyl-acrylic acid.

Methyl- β , β -naphthoyl-acrylate.—Five g. of the acid was dissolved in methyl alcohol and the solution saturated with hydrogen chloride. The ester crystallized in plates, m. p., 94-95°, and is soluble in acetic acid, chloroform or benzeue.

 β -p-Phenyl-benzoyl-acrylic Acid.—Five g. of maleic anhydride and 8 g. of diphenyl were dissolved in 50 cc. of benzene and 15 g. of aluminum chloride was added. The temperature was kept at 60–70° for 4 hours. Only a small amount of diphenyl and no benzoyl-acrylic acid were recovered and practically no tar was formed. Recrystallization from acetic acid gave yellow needles; m. p., 167–168°; yield, 80%. The acid is quite soluble in acetone, ether or ethyl alcohol and insoluble in cold benzene or toluene. The sodium salt is only slightly soluble in water.

Analysis of silver salt. Calc. for C₁₆H₁₁O₃Ag: Ag, 30.05. Found: 29.75.

Methyl β -p-Phenyl-benzoyl-acrylate.—Four g. of the acid was dissolved in methyl alcohol and after treatment with hydrogen chloride the solution was boiled for $^{1}/_{2}$ hour. The ester on recrystallization from ethyl alcohol melted at 73.5– 74° and is readily soluble in benzene, acetone or ether.

 β -p-Phenyl-benzoyl- α , β -dibromopropionic Acid.—Five g. of β -p-phenyl-benzoylacrylic acid was dissolved in hot acetic acid and bromine slowly added. It was immediately absorbed. The powder obtained by evaporating the solution was recrystallized from toluene; m. p., 180–181°. It was readily soluble in alcohol, acetone or ether and difficultly soluble in benzene or toluene.

Analysis. Calc. for C₁₆H₁₂O₂Br₂: Br, 38.8, Found: 38.35.

Identification of β -p-Phenyl-benzoyl- α , β -dibromopropionic Acid.—One g. of this acid was fused with 2 g. of potassium hydroxide for 10 minutes at 160° and p-phenyl-benzoic acid obtained from the product. This gives the formula for the original acid and for the bromine addition compound.

Methyl β -p-Phenyl-benzoyl- α , β -dibromopropionate.—Two g. of the acid was boiled for 30 minutes with methyl alcohol and hydrogen chloride. The ester on recrystallization from ethyl alcohol was white, m. p., $120-121^{\circ}$, and soluble in acetone, ether, acetic acid or benzene.

β-meso-Anthroyl-acrylic Acid.—Eight g. of maleic anhydride and 16 g. of anthracene were dissolved in 100 cc. of benzene and 24 g. of aluminum chloride was added slowly There was little action in the cold and the flask was warmed for 5 hours at 60–70°. After addition of hydrochloric acid, the solid was separated from the liquid and washed with benzene, yielding 15 g. of a light green product, which after recrystallization from acetic acid gave 10 g. of colorless crystals; m. p., 261°. This acid is soluble in acetone or chloro-

[Contribution from the Chemical Laboratories of Columbia University, No. 415]

THE RELATION BETWEEN MOLECULAR STRUCTURE AND ODOR IN TRI-SUBSTITUTED BENZENES. I. DERIVATIVES OF PARA-METHOXY-ACETOPHENONE

By Marston Taylor Bogert and Leo Patrick Curtin Received June 23, 1923

Introductory

So many well-known perfume substances among the tri-substituted benzenes possess the 1,3,4 arrangement that this has been called by Georg Cohn the "ideal configuration." Borneol, menthol, carone, fenchone, thujone, menthone, pulegone, camphor, carvacrol, thymol, eugenol, isoeugenol, safrol, piperonal, vanillin, acetovanillone, certain of the synthetic musks, and many others might be cited as illustrations of the fact that such an arrangement of the osmophore groups is of remarkably frequent occurrence in compounds possessing strong, agreeable odors.

In following this observation further, we have investigated various derivatives of p-methoxy-acetophenone, a substance which itself has a fine floral odor, and whose m-hydroxy derivative (2-hydroxy-4-methoxy-acetophenone), also known as peonol, occurs in the roots of the tree peony ($Paeonia\ moutan$) and has been employed in the perfume industry on account of its pleasant aroma.

Our purpose was to throw some additional light upon the connection between odor and structure in compounds of this type, by preparing new 1,3,4 derivatives and noting their odor.

One of the products we had in mind was the isomer of peonol, iso-acetovanillone (3-hydroxy-4-methoxy-acetophenone), but while our experiments were in progress, the article by Schneider and Kraft¹ appeared, describing the preparation of this compound by the action of sulfo-acetic acid upon guaiacol. As the authors make no mention of its possessing any noteworthy odor, the inference is that it has none.

The following derivatives of 4-methoxy-acetophenone were synthesized carrying an additional osmophore group adjacent to the methoxy: 3-nitro, 3-amino, 3-iodo, 3-cyano and 3-azido. Of these, all but the nitro derivative are new. All proved to be practically odorless.

In addition to the above, other new derivatives, carrying non-osmophores in Position 3, were prepared in the course of the investigation, as follows: aceto-amino, iodochloride, iodoso, *p*-nitrobenzalamino, sodium sulfonate, diazo perbromide, diazo-amino, amino-azo and 4-hydroxy-3-iodoso-acetophenone. These likewise were odorless, as might have been expected on account of their nonvolatility.

A tri-substituted benzene containing 3 osmophore groups in 1,3,4 re
Schneider and Kraft, Ber., 55B, 1892 (1922).

lation, therefore, is not because of that reason a perfume, even though its physical constants, such as boiling point, solubilities, etc., may be favorable. The connection between odor and constitution is not so simple then, and other factors must be involved which we hope may be discovered by a continuation of this investigation.

While p-methoxy-acetophenone itself is very stable and can be distilled at 258° without decomposition, its derivatives noted above are much more sensitive to the action of heat, especially in the presence of acid or alkali, and tarry by-products often seriously diminished the yields.

In carrying out reactions upon groups *ortho* to the methoxy, we encountered the well-known obstacle of steric hindrance.^{2,3,4} Thus, it was found impossible to hydrolyze the 3-cyano derivative to the corresponding amide or acid, or to obtain therefrom an imino ester; nor could we convert the 3-amino derivative into the phenol.

Many years ago, Victor Meyer⁵ pointed out that the hindering effect of the interfering group increased with its molecular weight. Our own observations lead us to suggest the following supplementary hypotheses.

- 1. The hindering effect of an interfering group diminishes as the molecular weight of the reacting group in the *ortho* position increases.
- 2. The hindering effect of an interfering group diminishes as the molecular weight of the foreign reacting molecule increases.

These tentative hypotheses are based upon the simple physical considerations of mass and inertia and are, of course, of a qualitative nature only. None the less, they may prove of service to others, as they have to us.

As an illustration of Hypothesis 1, the formation of the azido derivative from the diazo perbromide and ammonia may be cited. The methoxy group, with a molecular weight of 31, is crowded out to such an extent by the heavy diazo perbromide group (molecular weight, 268), that the azido compound is formed practically instantaneously in excellent yield, although the foreign attacking molecule has a molecular weight of only 17.

In confirmation of the second hypothesis are the failures to hydrolyze the cyano derivative by water or hydrogen dioxide, or to change it to an imino ester by anhydrous methyl alcohol and hydrogen chloride, and the inability to hydrolyze the diazonium chloride. In all these cases, the molecular weight of the reacting group was not far from that of the interfering one (methoxyl). On the other hand, reactions involving heavier foreign molecules were particularly satisfactory; as, for example, those with hydrogen iodide, tin, copper, potassium cyanide, and those participating in the formation of Schiff bases or diazo-amino derivatives.

² Biginelli, Gazz. chim. ital., 27, 347 (1897).

³ Cain and Nicoll, J. Chem. Soc., 81, 1440 (1902).

⁴ Cain, ibid., 83, 688 (1903).

⁵ Meyer, Ber., 28, 1260 (1895).

Experimental Part

The p-methoxy-acetophenone used in these experiments was prepared from anisole by a combination of the methods of Gattermann, Ehrhardt and Maisch⁶ and of Charon and Zamanos. The yield of pure product (m. p., $38-39^{\circ}$) was 61%. Charon and Zamanos report that their yields were those calculated. We were not so successful, as some unsymmetrical bis(p-anisyl)ethylene, small amounts of other products and considerable tar were always formed, although the acetyl chloride was added very slowly (2 hours) and the temperature was maintained below 10° . When petroleum ether was employed as solvent, in place of carbon disulfide, the yield was only 8%. With excess anisole as solvent, the yield was 30%, calculated to the anisole consumed in the reaction.

p-Methoxy-acetophenone Sodium Sulfonate.—p-Methoxy-acetophenone is not attacked by 95% sulfuric acid at 80°. Even fuming acid containing 15% of sulfur trioxide attacks it but slightly at laboratory temperature. It can be satisfactorily sulfonated, however, by great excess of stronger acid.

One hundred g. of fuming sulfuric acid containing $30\,\%$ of sulfur trioxide was cooled to $5\,^\circ$ and 25 g. of p-methoxy-acetophenone was added very slowly (30 minutes) with efficient stirring. After all the p-methoxy-acetophenone had been added, the stirring was continued for another half hour at low temperature, and the mixture then poured into 5 times its volume of ice-cold saturated salt solution. The sodium sulfonate soon began to separate, and after 20 minutes' further stirring the voluminous precipitate was filtered out; yield, nearly that calculated.

The salt formed large, snow-white, fatty leaflets, that turned pink when exposed to direct sunlight while still moist. Both the salt and the free acid were easily soluble in water.

Analysis. Calc. for C9H9O5SNa: S, 12.69. Found: 12.82.

Fusion of this sodium salt for 3 minutes with a low-melting mixture of sodium and potassium hydroxides completely destroyed it. The insignificant amount of phenolic product appeared to be mainly a catechol derivative, since with ferric chloride solution it gave immediately a deep green, turning red upon the addition of sodium carbonate. Evidently, the ether linkage was also ruptured in the fusion.

METHYL ESTER.—This was a colorless liquid prepared from the sodium sulfonate and dimethyl sulfate.

3-Nitro-4-methoxy-acetophenone has been described already by Stockhausen and Gattermann, who obtained it from o-nitro-anisole by the Friedel-Crafts reaction. Their yield was less than 9%. We find that high yields may be secured by the direct nitration of p-methoxy-acetophenone.

Fifty g. of p-methoxy-acetophenone was dissolved in 200 cc. of concd. sulfuric acid at laboratory temperature and the solution cooled to 0°. This solution was nitrated by the gradual (1 hour) addition of an ice-cold mixture of concd. nitric acid (containing ½ mole of nitric acid) with an equal volume of concd. sulfuric acid. Stirring was continued for 15 minutes after the addition of the mixed acids, and the solution was then poured into a liter of ice water. After standing for an hour, the precipitated nitro derivative was collected and crystallized from alcohol; yield, 95%. It formed slender, lemon-yellow, odorless needles; m. p., 99.5° (corr.). Stockhausen and Gattermann found this same melting point for their product.

Although it has been observed that o-methoxynitro derivatives are not readily reduced to the corresponding hydrazo compounds, the reaction was attempted with the

⁶ Gattermann, Ehrhardt and Maisch, Ber., 23, 1201 (1890).

⁷ Charon and Zamanos, Compt. rend., 133, 741 (1900).

⁸ Stockhausen and Gattermann, Ber., 25, 3521 (1892).

above nitromethoxy-acetophenone, following the procedure of Starke. Only tarry products resulted, nor could any benzidine derivative be isolated after treatment of the crude reaction product with coned. hydrochloric acid.

3-Amino-4-methoxy-acetophenone was prepared by reducing the above nitro derivative with tin and hydrochloric acid; yield, 74%. It crystallized from alcohol in large, flat, colorless, odorless hexagonal prisms; m. p., 102° (corr.); it was easily soluble in benzene, and moderately soluble in ether.

Analysis. Calc. for C₉H₁₁O₂N: C, 65.45; H, 6.67. Found: C, 65.68; H, 6.77.

ACETYL DERIVATIVE.—This was obtained by dissolving the amine in a slight excess of acetic anhydride and allowing the solution to stand for 2 or 3 days. It crystallized in colorless, rhombic prisms; m. p., 122.5° (corr.).

Analysis. Calc. for C₁₁H₁₃O₃N: C, 63.75; H, 6.33. Found: C, 63.68; H, 6.25.

Boiled with water, it was partially hydrolyzed. On crystallization from water, therefore, it showed a lower melting point, due to contamination with the free amine.

Benzal Derivative.—This was a sirupy substance that solidified only after long standing. When warmed slightly, it reverted to the sirupy form.

p-Nitrobenzal, Derivative.—This was obtained when the amine and p-nitrobenzaldehyde were heated at 110° for 15 hours.

Although a solid at laboratory temperatures, this product was not a crystalloid but a supercooled liquid. At room temperature, it was hard and brittle, but softened above 135° and was completely melted at 160°. The color ranged from deep red to yellow, depending upon the degree of subdivision of the solid. It was purified by dissolving it in boiling alcohol, in which it is but moderately soluble, and on cooling it separated in small droplets which soon solidified.

Analysis. Calc. for C₁₆H₁₄O₄N₂: C, 64.43; H, 4.70. Found: C, 64.18; H, 4.69.

Attempts to obtain the phenylhydrazine from the amine failed, in part due probably to intermolecular condensations of hydrazine and acetyl groups with formation of complex hydrazone types, leading finally to tars.

Similar lack of success attended our experiments for the production of a quinoline from the amine. Arsenic acid¹⁰ was used as the oxidizing agent, but the yield of the quinoline was exceedingly poor, and tars were the main products.

Before the publication of the article by Schneider and Kraft¹ reporting the preparation of iso-acetovanillone from guaiacol, we had made a number of futile attempts to produce the same compound from the above amine. The diazonium salt was boiled in aqueous solution, it was dropped cold into a mixture of sulfuric acid and sodium hydrogen sulfate at 140° and at 160°,¹¹¹ and it was added to a boiling solution of equal parts by weight of copper sulfate and water;¹² but no iso-acetovanillone was isolated in any of these experiments, only tarry substances being formed.

3-Iodo-4-methoxy-acetophenone, prepared from the amino derivative, through the diazo reaction, was purified by repeated crystallization from 50% acetic acid, after decantation from tarry by-products; yield, 55%. It was obtained as yellow, feathery, odorless needles, m. p., 103.6° (corr.), that rapidly became brownish in the light and were easily soluble in alcohol, chloroform, ether or glacial acetic acid.

Analysis. Calc. for C9H9O2I: C, 39.13; H, 3.26. Found: C, 39.29; H, 3.36.

When it was boiled for several hours with alcoholic potassium hydroxide solution, no phenol was formed.

⁹ Starke, J. prakt. Chem. [2] 59, 210 (1889).

¹⁰ Kueppel, Ber., 29, 704 (1896).

¹¹ Ger. pat., 95,339; Winther, I, 216.

¹² Ger. pat., 167,211; ibid., I, 211.

3-Iodochloride-4-methoxy-acetophenone, (ICI₂)(CH₃O)C₆H₃COCH₃.—When the iodo derivative was dissolved in chloroform and the solution saturated with dry chlorine, an unstable iodochloride was obtained in fine, bright yellow crystals.

This compound lost its chlorine so easily that it could not be obtained pure. In a closed vessel, the chlorine liberated displaced hydrogen of the molecule, and the only gas then found present was hydrogen chloride. The result was a mixture of products, which is now awaiting further examination, and which probably contains some of its chlorine in Position 6.

3-Iodoso-4-methoxy-acetophenone.—The freshly precipitated iodochloride was treated with 5 M potassium hydroxide solution. The product was a grayish white, putty-like, amorphous mass that decomposed suddenly when heated. Efforts to purify it by crystallization from various solvents were unavailing, as it always separated in a slimy, amorphous form.

3-Iodoso-4-hydroxy-acetophenone.—In the preparation of the above iodosomethoxy derivative, the clear alkaline filtrate was made acid by passing into it a current of sulfur dioxide. A precipitate resulted that was believed at first to be the iodonium iodide, ¹³ an assumption which was shown to be untenable because of the ready solubility of the substance in dil. aqueous alkali and the analytical results. The precipitation of the compound from its alkaline solution by sulfur dioxide also indicated the presence of a phenolic hydroxyl group, presumably formed by the action of the strong alkali used in attacking the iodochloride, the ether being saponified thereby, due to the acid groups ortho and para to it.

From 50% alcohol, the compound crystallized in long, pale yellow needles, that melted without decomposition at 243° when carefully heated, but decomposed suddenly when heated rapidly. It was easily soluble in alcohol or benzene, and moderately soluble in ether.

Analysis. Calc. for $C_8H_7O_3I$: C, 34.55; H, 2.54. Found: C, 33.58, 34.26; H, 2.62, 2.68.

3-Cyano-4-methoxy-acetophenone (3-Acetyl-6-methoxy-benzonitrile) was prepared from the amine by the usual Sandmeyer method; yield, 70%.

The product crystallized from alcohol in fine, pale yellow, odorless needles, m. p. 159.5° (corr.), that soon changed to a light orange-yellow color. It was moderately soluble in alcohol or ether, and dissolved readily in benzene.

Analysis. Calc. for C₁₀H₉O₂N: C, 68.55; H, 5.18. Found: C, 68.35; H, 5.27.

An attempt to prepare the amide from this nitrile by the action of alkaline hydrogen dioxide¹⁴ proved unsuccessful, the nitrile being recovered unchanged.

Efforts to saponify the nitrile to the corresponding acid were almost equally disappointing. Heating it with 70% sulfuric acid for several hours gave mainly tarry products, but a very small amount of a carboxylic acid was isolated, insufficient for purification, which melted with decomposition at 255°. Boiling the nitrile with concd. hydrochloric acid for 10 hours, heating it with 5 M potassium hydroxide solution for several hours, or fusing the sodium sulfonate with sodium formate, alike failed to yield the acid sought and gave only decomposition products.

Experiments were also conducted for the conversion of the nitrile into the imino ester by the action of dry hydrogen chloride and anhydrous methyl alcohol, but no reaction occurred, and the nitrile was recovered unaltered.

2-Methoxy-5-acetyl-diazobenzene Perbromide was precipitated at once when the calculated amount of bromine dissolved in hydrobromic acid was added to the diazonium chloride; yield, nearly that calculated.

¹³ V. Meyer, Ber., 27, 1592 (1894).

¹⁴ Radziszewski, *ibid.*, **18**, 355 (1885).

The compound formed pale yellow, flat needles (from cold alcohol), m. p., 68-70°, that decomposed on standing or on heating them with alcohol.

2-Methoxy-5-acetyl-azidobenzene, (CH₃O)(CH₃CO)C₆N₃.N₃.—Ammonium hydroxide solution was added with vigorous stirring to a fine suspension of the diazo perbromide in water.¹⁵ The azido compound was precipitated instantly as a mahogany-red mass which, after decolorization and recrystallization from dil. alcohol, was obtained in long, delicate needles of a peculiar faint pinkish buff color that darkened on standing and melted with decomposition at 87° (corr.). When heated rapidly, the substance exploded slightly above its melting point. It was freely soluble in alcohol or benzene, and also dissolved easily in ether; yield, 75%.

Analysis. Calc. for C₉H₉O₂N₃: C, 56.53; H, 4.74. Found: C, 56.33; H, 4.65.

The method of Culmann and Gasiorowski¹⁶ for the synthesis of azidobenzenes by the action of hydrochloric acid and stannous chloride upon the diazonium chloride was tried and found to be unsuitable for the production of this azide.

Griess¹⁷ has shown that certain azidobenzenes with a free para position rearrange to p-aminophenols when heated with 50% sulfuric acid. The azido derivative of p-methoxy-acetophenone described above, however, decomposed to a tar after only 15 minutes' heating with 25% acid.

2,2'-Dimethoxy-5,5'-diacetyl-diazo-aminobenzene, $(CH_3O)(CH_3CO)C_6H_3.N:N.NH.$ $C_6H_3(COCH_3)(OCH_3)$.—Ten g. of the 3-amino-4-methoxy-acetophenone was dissolved in 50 cc. of water and 20 g. of concd. hydrochloric acid, and the solution was well cooled and diazotized with the exact amount of sodium nitrite. To this diazo solution was added a solution of 10 g. of the same amine in 20 cc. of water and 6 g. of concd. hydrochloric acid, followed by a saturated aqueous solution of 35 g. of potassium acetate. The diazo-amino compound precipitated immediately. It was purified by boiling it in alcoholic solution with a decolorizing carbon, filtering the solution while it was still boiling hot, cooling quickly in an ice pack and filtering it promptly with suction. When the pale yellow solution was allowed to cool slowly, orange-colored needles formed that were contaminated with the isomeric amino-azo derivative described below; yield, 95%.

The pure product formed small, pale yellow needles, m. p. 178° (corr.), but was sparingly soluble in boiling alcohol and nearly insoluble in cold.

Analysis. Calc. for C₁₈H₁₉O₄N₃: C, 63.34; H, 5.57. Found: C, 63.10; H, 5.46.

2,2'-Dimethoxy-5,5'-diacetyl-4-amino-azobenzene.—The diazo-amino derivative was suspended in water and an equivalent amount of hydrochloric acid¹⁸ added. After standing at laboratory temperature for 3 days, the mixture had changed mainly to tarry products and only a small amount of the aminoazo derivative was secured. It formed dark red microscopic crystals (from 50% alcohol), m. p. $198-200^{\circ}$ (corr.), and proved to be an extremely feeble base, being insoluble in 10~M hydrochloric acid, but soluble in 13~M with a greenish blue color.

Analysis. Calc. for C₁₈H₁₉O₄N₃: C, 63.34; H, 5.57. Found: C, 63.18; H, 5.44.

Summary

- 1. Tri-substituted benzenes carrying osmophores in 1,3,4 arrangement are not always odorous, even when sufficiently volatile.
 - 2. Although 4-methoxy-acetophenone is itself a perfume substance
 - 15 Griess, Ann., 137, 68 (1866).
 - ¹⁶ Culmann and Gasiorowski, J. prakt. Chem., [2] 40, 99 (1889).
 - 17 Griess, Ber., 27, 313 (1894).
 - ¹⁸ Friswell and Green, J. Chem. Soc., 47, 920 (1885).

the introduction of the osmophores NO₂, NH₂, N₃ or CN, in Position 3 results in odorless products.

- 3. Certain new hypotheses are advanced concerning steric hindrance.
- 4. The following new compounds are described: the 3-sulfo, 3-amino, 3-acetamino, 3-p-nitrobenzalamino, 3-iodo, 3-iodochloride, 3-iodoso and 3-cyano derivatives of 4-methoxy-acetophenone; and from the 3-amino, the corresponding diazo perbromide, azido, diazo-amino and amino-azo derivatives; also the 3-iodoso-4-hydroxy-acetophenone.
- 5. Some improved methods of preparation have been developed for compounds previously known.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE KETENIC DECOMPOSITION OF METHYLETHYL KETONE

By Charles DeWitt Hurd and Cyril Kocour Received June 25, 1923

It has recently been demonstrated that ketene can be prepared in excellent yields¹ merely by heating acetone vapors in a suitable apparatus. With this in view, methylethyl ketone was put to the same test. It can evidently decompose in two ways: $CH_3-CO-C_2H_5 \longrightarrow CH_2:CO + C_2H_6$; or $CH_3-CH_2-CO-CH_3 \longrightarrow CH_3-CH:CO + CH_4$. If ketene were formed, it would not be a profitable process unless the yield were better than that obtained in the decomposition of acetone.² However, if methyl ketene were formed, the reaction would be one of great interest regardless of the yield, inasmuch as methyl ketene is unusually difficult to prepare.

The literature that deals with methyl ketene is very limited. Staudinger³ prepared it in ethereal solution in 6 to 8% yield from α -bromopropionyl bromide and zinc shavings. No other positive statements are on record, although a few negative items bear witness to the difficulty of its isolation. One such is given by Ott.⁴ In his discussion of the ketonic decomposition of β -lactones, he observed that $(CH_3)_2C-C(CH_3)-COOH$ de-

composed at 110-113° into acetone, carbon suboxide, and an oil in approximately 80-

¹ Hurd and Cochran, This Journal, 45, 515 (1923). A repetition of the experiment was made in this Laboratory by Mr. J. W. Kern who obtained 18.5 g. of purified acetanilide from 28 g. of unrecovered acetone, a yield of 28.3%, in contrast to the yield of 17.5% reported in the original article. The only change in the apparatus was the use of tight-fitting rubber stoppers in place of corks, wherever possible; where corks were used they were well softened and painted with water glass inside and outside 1 day before use. As in the original report, the gas burners were giving their full blast. It is now thought that the temperature 600°, which was originally reported, is somewhat lower than the true temperature of the furnace.

² Methylethyl ketone is nearly as inexpensive as acetone.

³ Staudinger, Ber., 44, 535, 541 (1911).

⁴ Ott, Ann., 401, 159 (1914).

85% yield. Methyl ketene was reported to be absent. This was interesting, inasmuch as the lower homolog, (CH₃)₂C—CH—COOH, also formed acetone, and carbon sub-

oxide at its melting point. In this case, acetic acid was also isolated.

Very few data are obtainable concerning the behavior of methylethyl ketone at high temperatures. At least, it is stable at temperatures that do not exceed 450°. Other ketones, such as acetone, diethyl ketone, dipropyl ketone and methylpropyl ketone behave similarly.⁵

Poma and Nesti⁶ have studied the action of the silent electric discharge upon the vapor of methylethyl ketone. Of the gaseous decomposition products, they reported 43.6% of methane (or ethane), 32.8% of carbon monoxide, 12.5% of ethylene (or acetylene) and 10.2% of hydrogen. The liquid products were not analyzed completely, but sym-dimethyl-acetonyl acetone was shown to be present.

Ketene was found in our experiments, but we obtained no evidence of the formation of methyl ketene. This seems to be direct evidence that only the first of the two possible reactions mentioned above takes place. However, it is entirely possible that methyl ketene is also formed, and that it decomposes at the high temperature of the experiment. This problem is being studied further and will be discussed in a later paper.

Condensation products of methylethyl ketone were to be expected. We found that they constituted between 4 and 5% of the distillate. The remaining 95% was unchanged methylethyl ketone. The work of Bodroux and Taboury and of Becker and Thorpe would lead us to expect that methyl-5-heptene-4-one-3, C₂H₅-CO-CH: C(CH₃)-C₂H₅, would be contained in this mixture. No attempt, however, was made to determine the exact nature of the small amount of higher-boiling material obtained in our experiments.

Because of the fact that both ketene and methyl ketene are gases that polymerize easily, no attempt was made to isolate them but, instead, reagents were sought that would differentiate between the two. The following were used: aniline, toluidine, and water.

Experimental Part

Commercial methylethyl ketone was purified by several fractional distillations. The portion that was finally used, distilled almost completely¹⁰ between 79° and 80°.

The apparatus was similar in its essential features to that described by

- ⁵ Senderens, Compt. rend., 149, 996, footnote, (1909); Bull. soc. chim., [4] 5, 484 (1909).
 - ⁶ Poma and Nesti, Gazz. chim. ital., [2] 51, 89 (1921).
 - ⁷ See Experimental Part, p. 2170.
 - 8 Bodroux and Taboury, Bull. soc. chim., [4] 3, 831 (1908).
 - ⁹ Becker and Thorpe, J. Chem. Soc., 121, 1303 (1922).
- ¹⁰ Brunel [This Journal, **45**, 1338 (1923)] reported that very pure methylethyl ketone boils at 79.37° at 755 mm.

Hurd and Cochran. It is of fundamental importance that all joints be made as free from leaks as possible. Rubber stoppers were used in the cooler parts of the apparatus, where they were not in contact with methylethyl ketone. The corks used elsewhere were selected ones, well softened, and carefully fitted. They were painted with water glass, inside and out, and allowed to stand for some time before use in order to permit the water glass to harden before pressure was applied to it. Another difference in the apparatus was the use of an oil-bath, heated to about 120°, in place of the boiling water-bath. This was found necessary in order to effect immediate vaporization of the ketone as it dropped into the 500cc. flask. The burners beneath the combustion furnace were adjusted for a flame about $^3/_4$ the size of the full blast. The temperature, roughly measured in the middle of the furnace with a quartz thermometer, was 600° .

About 80 g. of methylethyl ketone was used in each run. The duration of the experiment ordinarily ranged between 1.5 and 2 hours. The ketone was added at such a rate that between 50 and 60 g. of distillate was recovered. The yields of ketene, based upon the methylethyl ketone that was not recovered, varied between 1 and 3.5%. In the report that follows, all duplicate runs that did not contribute essentially independent data have been omitted for purposes of brevity.

Reaction with Aniline

Eighty g. of methylethyl ketone was passed through the combustion tube; 56 g. of distillate was collected; therefore, 24 g. of the ketone may have decomposed. Ten g. of freshly distilled aniline was placed in the reaction flask with 50 cc. of absolute ether. At the end of the experiment the excess of aniline was removed by distillation with steam. The water solution of the non-volatile portion was evaporated, and the residue was recrystallized from a mixture of ethyl acetate and ligroin. About 0.8 g. of acetanilide, m. p., 112°, was isolated.

There was no indication of the presence of propionanilide, which indicates that no methyl ketene reached this part of the apparatus. However, a very small amount of material that melted at 79° was isolated. As yet it is unidentified, but further work with this compound is in progress. It is best recrystallized from hot ligroin (100–110°). It possesses about the same degree of solubility in hot water as acetanilide, for no separation by fractional crystallization from this solvent could be effected.

Reaction with para-Toluidine

About 10 g. of p-toluidine (m. p., 44-45°) was dissolved in absolute ether and placed in the reaction flask. A second reaction bottle containing aniline was placed in series to ascertain whether or not any ketene escaped reaction in the first flask. Only a trace of acetanilide was found, which proved that the reaction of ketene with toluidine is nearly instantaneous.

Of the 80 g. of ketone used originally, 60 g. was recovered. At the completion of the run, the excess of toluidine was removed by distillation with steam. The non-volatile portion was filtered while still hot, and the filtrate was then cooled in ice. A

¹¹ Ref. 1, p. 519.

voluminous white precipitate appeared which was collected and dried. Without further purification, it melted at 142°; yield, 0.8 g.; this represents a 2% yield of ketene. This product was resolved into 2 fractions by fractional crystallization from ligroin in which was dissolved a little ethyl acetate. The more insoluble fraction melted at 145°. Its identity was proved without question to be p-acetotoluidide by comparison with a known sample. The latter was prepared by the action of 1 cc. of acetyl chloride upon 1.5 g. of p-toluidine. The resultant product was heated to about 150° for a time, then cooled, washed with water, collected and dried; m. p., 145°. After one recrystallization from a mixture of ethyl acetate and ligroin, it melted at 146–147°. A mixture of this and the ketene product melted at 145–146°.

From the more soluble fraction was resolved a small quantity of a white crystalline compound that melted at 106°. This is probably similar to the compound that melts at 79° formed during the reaction with aniline. Work is being continued with both compounds.

At first, it was thought that it was o-acetotoluidide, but a mixed melting-point determination with a known sample showed the incorrectness of such an assumption. The mixture melted between 70–80°. The known sample was prepared by the action of 5.2 g. of acetic anhydride upon 10.7 g. of o-toluidine. The mixture was heated with a small flame for 2 hours, cooled, and recrystallized from a mixture of benzene and ligroin. It was then recrystallized from ligroin (100–110°), a solvent that fails to dissolve the para compound. The pure crystals melted at 109–110°.

Reaction with Water

A mixture of an excess of water with ether was placed in the first reaction flask. The second contained aniline and ether. Of the 80 g. of methylethyl ketone used, 52 g. was recovered. The slowness of the reaction between ketene and water was evidenced when 0.87 g. of acetanilide was isolated from the second reaction flask.

After the evaporation of ether from the mixture in the first flask a little phenolphthalein was added and the acid solution neutralized with 0.05~N sodium hydroxide solution. The solution of salt was then evaporated and dried. It weighed 1.144~g. To determine whether this salt was sodium acetate or sodium propionate, 1~g. of it was treated in 63% alcoholic solution with 1~g. of p-nitrobenzyl bromide. The product which resulted was p-nitrobenzyl acetate; after 2~ecrystallizations from alcohol it melted at 73-75°.

The total yield of ketene in this run was 3.5%, based upon the ketone that was not recovered.

The Distillate

One hundred and sixty g. of distillate, which was collected by the vertical condenser, was fractionated thrice; 43 g. boiled between 75° and 77°; 82 g. between 77° and 80°; 28 g. between 80° and 85°; 3.5 g. between 85° and 125°; 2 g. between 125° and 150°; and a foully smelling liquid which weighed 1.5 g. remained. The 7 g. of material that boiled above 85° represents 4.4% of the total. The rest was methylethyl ketone.

The two U-tubes that were placed between the condenser and the first reaction bottle collected but a small quantity of liquid that possessed an exceedingly pungent odor.

Summary

When methylethyl ketone is passed through a tube at 600°, ketene is formed in small yields. The presence of methyl ketene could not be demonstrated.

12 Two values for the m. p. of p-acetotoluidide are listed. Riche and Berard [Ann.,
 129, 77 (1864)] give 145°, whereas Feitler [Z. physik. Chem., 4, 76 (1889)] gives 153°.
 13 Reid, This Journal, 39, 126 (1917).

Ketene reacts much more slowly with water than with aniline or with toluidine.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. III. PREPARATION AND PROPERTIES OF THE OXIDE OF PLATINUM OBTAINED BY THE FUSION OF CHLOROPLATINIC ACID WITH SODIUM NITRATE:

By Roger Adams and R. L. Shriner²
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In two previous papers³ the platinum oxide obtained by the fusion of chloroplatinic acid and sodium nitrate has been shown to be an excellent catalyst in the reduction of organic compounds. This method for the preparation of an oxide of platinum is new. The chemical nature of this oxide and a quantitative study of the best conditions for its preparation have not yet been described.

This communication discusses (1) the best fusion temperature for preparing the platinum oxide of highest catalytic activity; (2) the quantitative analysis of various samples of the catalyst prepared at different temperatures; (3) the general chemical properties of the oxide; (4) a comparison of the activity as a catalyst of the oxide of platinum prepared from chloroplatinic acid by fusion with sodium nitrate and by fusion with the nitrates of other metals; (5) a comparison of the catalytic activity of the oxide made by the sodium nitrate fusion method with the oxides of platinum prepared by methods which have already been described in the literature.

The Temperature of Fusion

The best qualitative conditions for preparing the oxide of platinum have been described; a large excess of nitrate is advisable, and a rather high temperature of fusion gives a more active catalyst. During the fusion fumes of nitrogen dioxide are evolved and the oxide of platinum is precipitated. It is probable that the following reactions take place: $6NaNO_3 + H_2PtCl_6 \longrightarrow 6NaCl + Pt(NO_3)_4 + 2HNO_3$; $Pt(NO_3)_4 \longrightarrow PtO_2 + (NO_2)_4 + O_2$.

- ¹ Part of the chloroplatinic acid used in this investigation was purchased with the aid of a grant from the Bache Fund of the National Academy of Sciences. For this aid the authors are greatly indebted.
- ² This communication is an abstract of a thesis submitted by R. L. Shriner in partial fulfilment of the requirements for the Degree of Master of Science in Chemistry at the University of Illinois.
 - 3 (a) Voorhees with Adams, This Journal, 44, 1397 (1922).
 - (b) Carothers with Adams, ibid., 45, 1071 (1923).

The standard procedure used to determine the temperature of fusion that gives the most active catalyst was similar to that previously used. A solution of 4.2 g. of chloroplatinic acid in 10 cc. of water was mixed with 40 g. of c. p. sodium nitrate and evaporated to dryness in a casserole or beaker. The mass was then heated with an ordinary Bunsen or Meker burner until fusion took place. The mixture and melt were stirred continuously with a thermocouple encased in a Pyrex glass tube and the temperature was read on a pyrometer. After the fusion was complete, the melt was allowed to cool and treated with water until the filtrates were free from nitrates and nitrites. The oxide was then dried in a desiccator and weighed in order to determine the yield. Portions of this dried material were weighed for the reduction experiments.

The temperatures used in the fusion for the preparation of the oxide ranged from 310°, the lowest possible temperature, to 700°, a temperature which is bright redness and cannot be reached with two Bunsen burners; it is necessary to use at least one Meker burner and one Bunsen burner.

In the first experiment the mixture was heated, during the course of 5 minutes, to 270–280° at which temperature melting began. The temperature was gradually raised, the reaction mixture reaching 300° at the end of about 8 minutes, and evolution of nitrogen dioxide commenced. The heating was continued until at the end of 10 minutes it reached 310°, then it was increased rapidly to 320° where it was held until the end of 20 minutes, after which the mixture was allowed to cool. Gas was evolved slowly from the time a temperature of 300° was reached and at the same time a brown precipitate gradually appeared. The reaction mixture was then worked up as described and the yield of 0.3 g. (1.69 g. is the theoretical amount) of platinum oxide was obtained. It is obvious that under these conditions the reaction was not nearly complete.

In the second experiment, the mixture was heated more rapidly, the fusion reaching 350-370° in 10 minutes. At this temperature a very vigorous evolution of oxides of nitrogen took place. The temperature was raised to 400° by the end of 15 minutes, by which time the evolution of gas had slackened. The temperature was then held at 400° until 20 minutes had elapsed when heating was discontinued. Evolution of gas had practically stopped at the end of this time. The precipitation of the oxide of platinum was rapid from 350° on. The yield of dry product was 1.4 g.

In the subsequent experiments sufficient heat was applied so that a temperature of 350–370° was reached in 10 minutes. The temperature was then raised and controlled over the period between 10 and 25 minutes. In each case, at the end of 15 minutes the evolution of gas had almost stopped. In Expt. 3, a temperature of 400° was reached at the end of 15 minutes and a temperature of 490–500° at the end of 20 minutes, at which point it was maintained until 25 minutes had elapsed.

In Expt. 4 the temperature was about 500° at the end of 15 minutes, 580° at the end of 20 minutes, and was maintained at 590-600° until 25 minutes had elapsed.

In Expts. 5 and 6 the conditions were similar to those in Expts. 3 and 4, except that in Expt. 5 a temperature of 650°, and in Expt. 6 a temperature of 700° was reached at the end of 20 minutes and maintained at this point until 25 minutes had elapsed. At a temperature of 650° and higher the melt boiled.

The yield of oxide in Expts. 3, 4, 5, 6 was practically quantitative. The only difference in the oxides obtained at the different temperatures

was in their appearance, the color changing from light brown in Expts. 1 and 2 to a very deep brown in Expt. 6.

In order to determine the relative activity of the various samples of oxide as catalysts, standard experiments were carried out with each sample in the reduction of two different types of organic compounds, benzaldehyde in the presence of a trace of ferrous chloride, and maleic acid. The procedure was to dissolve 20 g. of benzaldehyde or 20 g. of maleic acid in 150 cc. of 95% alcohol. To the benzaldehyde solution in each case, was added 1 cc. of 0.0001~M ferrous chloride. The solutions were reduced with 0.25~g. of catalyst in exactly the same manner as described in a previous paper. Table I gives the time for the reduction in each case.

Table I

Comparison of Catalytic Activity in Reduction Experiments of Samples of
Oxide made at Different Temperatures

Catalyst sample	Maximum temperature of fusion °C.	Time for reduction in minutes after reduction starte Benzaldehyde Maleic a		
1	310-320	40		
2	390-400	22	10	
3	490-500	10	11	
4	590-600	11	19	
5	650	20	17	
6	700	20	16	

The lag in the conversion of the platinum oxide to platinum black differed in each sample of the catalyst. It has not been taken into account in Table I but is shown in Table II. To find the total time, therefore, which is necessary for the reduction of benzaldehyde or maleic acid from the time the platinum oxide catalyst was added, it is necessary to add to the time given in Table I the corresponding lag time given in Table II.

Table II

Comparison of Time of Reduction to Platinum Black of Samples of Oxide Made at Different Temperatures

Catalyst sample	Maximum temperature of fusion ° C.	Time elapsing before was reduced to pla Benzaldehyde Min.	platinum oxide tinum black Maleic acid Min.
1	310-320	10	
2	390-400	5	2
3	490-500	1	1
4	590-600	2	3
5	650	7	5
6	700	11	17

These experiments show that a temperature of about 500° is most satisfactory for the fusion in order to obtain a catalyst of maximum activity and minimum lag. For this temperature one Bunsen burner turned on as high as possible was necessary. They also show that any sample

of catalyst may have a slightly variable lag depending upon the compound to be reduced; it may be possible, however, that this is due to slight changes in the conditions of the experiment. It is difficult to determine the lag accurately so that little importance can be given to slight differences in these values. In the previous papers describing the use of this catalyst, reactivation with air has been recommended in order to get the maximum speed of reduction of the organic compounds. It has been found since the publication of the first two papers that reactivation of the catalyst with oxygen instead of with air, as suggested by Willstätter⁴ has a much greater effect than had been anticipated. It is advisable, therefore, whenever using this catalyst, to reactivate by the latter method just mentioned. It is conceivable that in the reduction of a few types of organic compounds this would not be possible, but in the large majority it is possible, and will greatly cut down the time of the reaction.

The results on the activity of the platinum oxide catalyst made at different temperatures differ from those described in the first paper by Voorhees and Adams. This discrepancy in regard to the proper temperatures of preparation and speed of reduction is due to the fact that the reduction of benzaldehyde was chosen as a standard for the determination of the efficiency of the catalyst. At that time the tremendous effect of small amounts of certain metallic salts upon the activity of the platinum catalyst in the reduction of aldehydes was not known and consequently care was not taken to use platinum catalyst from the same source in every experiment.

Quantitative Analysis

Qualitative tests showed that the oxide of platinum obtained in the manner described contained a certain amount of water which probably was taken up during the washing to remove the alkali salts; the oxide also contained small amounts of alkali salts which were included and could not be washed out. The quantitative analyses showed the oxide to be PtO₂.H₂O.

The general procedure for the quantitative analyses was to heat weighed samples (about $0.5~\rm g$.) that had been previously well dried in a vacuum desiccator, to bright redness in a porcelain boat in a glass tube heated by an electric combustion furnace. Carbon dioxide was passed through continuously during the heating and the water that was driven off was absorbed in a sulfuric acid tube. After about 1 hour at bright redness no more moisture was evolved, the bulb was removed and the weight of water determined. The carbon dioxide was now stopped and hydrogen was passed over the red-hot residue in order to reduce the oxide to metallic platinum. This procedure was continued for 1.5 hours when no more moisture was formed. The boat was then allowed to cool and was weighed.

⁴ Willstätter, Ber., 54, 113 (1921).

The value thus obtained represented metallic platinum plus any alkali salts which were present. The residue was boiled with dil. sulfuric acid,⁵ the platinum filtered, dried and weighed. This treatment extracted practically all of the alkali salts.

It was found also that the catalyst contained a small amount of glaze from the porcelain casserole when such a vessel was used for the fusion. This was determined by dissolving a sample of the oxide in constant boiling hydrobromic acid, filtering the solution through a Gooch crucible and weighing the insoluble residue. This glaze averaged about 0.0025 g. in each 0.5g. sample and did not vary appreciably in the various samples of oxides.

The completed results on the analysis of each of the samples of catalyst, prepared at the various temperatures, are given in Table III.

Table III

Quantitative Analyses of Samples of Oxide Made at Different Temperatures

Temperature °C.	% Pt	% H ₂ O	% Alkali salts
390-400	78.90	7.13	2.22
490-500	79.80	7.37	1.72
590-600	78.00	9.16	3.56
650	79.80	8.83	3.66
700	79.40	8.06	4.80

Calc. for PtO2.H2O: Pt, 79.95; H2O, 7.34.

It may be seen that the amount of alkali salts varied with each preparation and particularly that the amount of alkali salts increased with the higher temperatures. Moreover, it is noticeable that the moisture content was somewhat higher with the oxides made at the higher temperatures. Although the analyses vary somewhat from the calculated results, they check much more closely with the theoretical values than many of the analyses of the oxides of platinum prepared by other investigators. The analyses leave no doubt as to the constitution of the oxide.

Properties of the Oxide

The physical and chemical properties of this oxide of platinum are interesting. It has already been mentioned that the color varied with the temperature at which the fusion was made. At the lowest temperature it was a very light brown and darkened gradually until at the highest temperature it was a very deep brown. It is probable that the difference in the color is due merely to a difference in the size of particles. A microscopic examination showed that the oxide is in every case non-crystalline in character and is composed of amorphous, approximately round granules.

The oxide dissolved only slightly in hot aqua regia even after long heating. It was insoluble in boiling coned. nitric acid and only slightly, or

⁵ Wöhler and Martin, Z. Elektrochem., 15, 132 (1909).

at least only slowly, soluble in boiling concd. hydrochloric acid. On the other hand, constant boiling hydrobromic acid dissolved it completely and instantly in the cold with the evolution of bromine and the formation of bromoplatinic acid which could be readily precipitated as the red potassium salt.⁶ By boiling it with 10% hydrobromic acid, solution was readily effected. It seems probable that the hydrobromic acid first reduces the dioxide to the monoxide which is dissolved with the formation of platinous bromide and then reoxidized by the bromine to the platinic bromide. Dilute or concd. hydrochloric acid had very little effect alone, but when a very small amount of sulfur dioxide was bubbled through dilute hydrochloric acid this mixture dissolved the platinum oxide rapidly and completely upon warming. In this case the reduction of the dioxide to the monoxide undoubtedly took place first before solution resulted. Other reducing agents with the dilute hydrochloric acid would undoubtedly produce the same effect.

The oxide caused the immediate decomposition of hydrogen peroxide without itself being apparently changed. When boiled with ethyl alcohol out of contact with air, the oxide was gradually reduced and acetaldehyde was formed.

Effect of the Nature of the Nitrate on the Activity of the Catalyst

All of the nitrates of the other alkali metals and of the alkaline earth metals fuse below 650°. These were, therefore, substituted for sodium nitrate in the fusion of the chloroplatinic acid. The oxides thus obtained were compared as catalysts by studying the reduction of benzaldehyde in exactly the same manner as previously described.

The procedure for these fusions was essentially the same as with sodium nitrate except that 3 g. of chloroplatinic acid and 20 g. each of the nitrates were used. The temperature was determined in a similar manner and the melt also treated similarly. The yields of product were quantitative in every case. In Table IV the results of these experiments are given.

Table IV

Comparison of the Catalytic Activity in Reduction Experiments of Samples of
Oxide by the Use of Various Nitrates

Nitrate	М. р. °С.	reduction of T benzaldehyde after reduction started Min.	Time for reduction of oxide to platinum black Min.	Temp. of fusion ° C.
LiNO ₃	253	12	9	490-500
NaNO ₃	312	10	1	490-500
KNO ₃		25	3	490-500
Ca(NO ₃) ₂	561	80	58	500-530
$Ba(NO_3)_2$	575	135	28	600-630
Sr(NO ₃) ₂	645	No reduction		630-640

⁶ Biilmann and Anderson, Ber., 36, 1566 (1903).

The lithium nitrate worked very satisfactorily in the fusion and yielded an active catalyst. It is noticeable, however, that the oxide produced is reduced to platinum black more slowly than that obtained by fusion with sodium nitrate.

The potassium nitrate was not so satisfactory as sodium nitrate. During the evaporation of the mixture of chloroplatinic acid and potassium nitrate to dryness, excessive foaming took place caused probably by the precipitate of potassium chloroplatinate. The oxide of platinum was produced in good yields but was not so active a catalyst as that obtained by the use of sodium nitrate.

Calcium nitrate itself decomposes just above its melting point into calcium nitrite and then into calcium oxide so that during the fusion with chloroplatinic acid the melt became very thick and viscid. The catalyst produced was very light yellow in color and did not resemble the oxide obtained by the fusion with the alkali metal nitrates. It was rather fluffy in appearance. It seems probable that this was an oxide of the formula PtO₂.2H₂O, since it resembled in appearance this substance as made by a method described in the literature and also in its catalytic activity in reduction experiments. The production of this substance could be explained by the primary formation of the calcium oxide which would precipitate the platinum oxide just as sodium hydroxide precipitates it from the chloroplatinic acid.

Both barium and strontium nitrates melt at so high a temperature that the platinum chloride, for the most part, is decomposed to metallic platinum before the fusion occurs, and hence the products from these fusions would not be expected to be so active as catalysts. That obtained from the barium nitrate caused the reduction of benzaldehyde only very slowly, and that from the strontium nitrate caused no reduction at all.

Comparison of this Catalyst with Platinum Oxides Made by Other Methods

A discussion^{3a} has already been made of the reasons for attempting to use the oxides of platinum as catalysts in the reduction of organic compounds. None of the oxides is as conveniently prepared as the oxide prepared by the fusion of sodium nitrate and chloroplatinic acid. Wöhler and Martin⁵ gave explicit directions for the preparation of a number of the oxides and these directions have been followed. These investigators, however, did not mention yields, a point of considerable importance when the oxides are to be used as catalysts. Most of the methods consisted in wet precipitation, and as slight changes in condition might make a considerable difference in the activity of the product as a catalyst, two different samples of each oxide were prepared.

In Table V a summary of the results of the use of PtO2, PtO2.2H2O,

 Pt_2O_3 , Pt_3O_4 and $Pt(OH)_2$ in reduction experiments is given. Since the majority of the oxides were comparatively non-active catalysts, smaller amounts of maleic acid and benzaldehyde were reduced than when the oxide catalyst prepared by fusion was used.

TABLE V

Comparison of Catalytic Activity in Reduction Experiments of Fusion Oxide and Various Platinum Oxides Made in Other Ways

					duction includi	
	% of oxide			ction of oxide	to platinum b	lack
	ostained from				enzaldehyde (1	
	the chloro-	oxide	(1)	0 g.)	(9.5 g	g.)
	platinic acid	used	Sample	Sample	Sample	Sample
Oxide	used	G.	1	2	1	2
Fusion oxide	100	0.25	10 m.		7 m.	
PtO_2	51	.24	4 h.	1.25 h.	50 m.	69 m.
$PtO_2.2H_2O$	60	.30	5.66 h.	5.0 h.	40 m.	60 m.
Pt_2O_3,\ldots	6	.23	5.5 h.	No red.	3.5 h.	4.75 h.
Pt_3O_4	82	.23	2.3 h.	2.6 h.	1.41 h.	1.33 h.
$Pt(OH)_2$	14	.24	No red.	No red.	8.41 h.	32 h.

It is noticeable that the yields of these other oxides were not nearly so satisfactory as that obtained by the fusion method. The oxides, moreover, were not nearly such active catalysts and the same oxide varied in activity from sample to sample even though prepared by the same directions. One of the distinct advantages in the fusion oxide is that a catalyst of standard activity is obtained.

The oxide Pt_3O_4 was made by the fusion of chloroplatinic acid with sodium carbonate. The oxide was formed in satisfactory yields distinctly greater than those of the oxides prepared by any of the other methods except that by fusion with sodium nitrate. The activity as a catalyst, however, was not as great as with PtO_2 or $PtO_2.2H_2O$.

In Table V the times recorded include both the time of reduction of the oxide to platinum black and the time of reduction of the compound. Since the last 3 oxides in the table were black at the beginning, it was very difficult to determine the exact point at which a platinum black was formed and consequently in order to have uniform results for comparison the total time was recorded.

Summary

- 1. The fusion of sodium nitrate and chloroplatinic acid has been carried out at various temperatures between 310° and 700°. The various samples of oxide of platinum produced were tested as catalysts in the reduction of maleic acid and benzaldehyde. It was shown that the oxide prepared at about 500° gave the best results in the reduction experiments.
- 2. A quantitative analysis of the oxide has shown it to have the composition $PtO_2.H_2O.$
- 3. This oxide is insoluble in aqua regia, concd. nitric or concd. hydrochloric acid. It is readily soluble in hydrobromic acid or hydrochloric

Identification of the Di-2,4-xylyl-dibromo-ethane.—One g. of the bromine addition compound was fused with 2 g. of potassium hydroxide for 10 minutes at 135° . The product on acidification gave 2,4-dimethyl-benzoic acid. This also identifies the dixylyl-ethylene as di-2,4-xylyl-ethylene.

Di-2,4-xylyl-ethylene (cis).—Two g. of the trans compound was dissolved in methyl alcohol and allowed to stand in sunlight for a week. A great deal of the original material was unchanged, but on evaporation of the alcohol the last precipitate was an oil which on recrystallization from ligroin gave colorless, needle-shaped crystals; m. p., 65–65.5°. These crystals are soluble in acetone, ether, benzene or chloroform. The bromine addition compound was made in acetic acid solution and was identical with that made from the trans form. A mixed melting point was not lower.

Di-p-phenyl-benzoyl-ethylene (trans).—A mixture of 8 g. of fumaryl chloride, 12 g. of diphenyl, 60 cc. of benzene, and 20 g. of aluminum chloride was kept at room temperature for 1 day. After decomposition of the intermediate compound and removal of the benzene and diphenyl by distillation with steam, the product was washed with hot benzene and a yellow powder was left; m. p., 247.5-248°. It is slightly soluble in benzene, and acetic acid and somewhat more soluble in chloroform. The solution in chloroform was exposed to 36 hours' sunlight but no product other than the original trans compound was obtained.

Di-p-phenyl-benzoyl-dibromo-ethane.—One g. of the di-p-phenyl-benzoyl-ethylene was dissolved in chloroform and bromine added. The color disappeared gradually and on evaporation of the solution a white solid, m. p., 218–218.5°, was obtained. This compound is slightly soluble in acetone or ether. Both this substance and the original ethylene derivative are assumed to contain the p-phenyl-benzoyl group.

Analysis. Calc. for C28H20O2Br2: Br, 30.3. Found: 29.85.

This work was done under the direction of Professor F. B. Allan and was made possible through assistance in the form of a Studentship received from the Research Council of Canada.

Summary

- 1. Rubidge and Qua's method for the preparation of diphenyl-phthalide was found not to be applicable to the preparation of diphenyl-croton lactone from maleic anhydride. An attempt to prepare this lactone from the anhydride of β -benzoyl-acrylic acid and acetic acid was also unsuccessful.
- 2. Several unsaturated keto acids have been prepared from maleic anhydride, and some of their addition compounds have been obtained. Some of these unsaturated keto acids readily formed addition compounds with bromine; others did not.
- 3. Using fumaryl chloride, several unsaturated diketones have been prepared as well as their bromine addition compounds. In two of these the yellow *trans* form has been changed to the colorless *cis* form by exposure to sunlight. The behavior of ditoloyl-ethylene seems to be peculiar; further work will be done on this.

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form and slightly soluble in benzene, toluene or acetic acid. It did not react with bromine in either cold or hot acetic acid solution, and fusion with potassium hydroxide at 250° gave no decomposition. It is assumed to be the *meso*-anthroyl derivative. The sodium salt and the ammonium salt are only slightly soluble in water.

Analysis of ammonium salt. Calc. for C18H15O3N: N, 4.77. Found: 4.82.

Methyl β -meso-Anthroyl-acrylate.—Three g. of β -meso-anthroyl-acrylic acid was dissolved in 100 cc. of methyl alcohol and hydrogen chloride added. After the solution had stood for 2 days, colorless plates crystallized and these after recrystallization from acetic acid gave needles 2 cm. long; m. p., 149.5–150°. The ester is soluble in acctone, chloroform or benzene and less soluble in acetic acid.

Di-p-toluyl-ethylene (trans).—To 7 g. of fumaryl chloride and 50 cc. of toluene 20 g. of aluminum chloride was added slowly. The reacting substances were kept at room temperature overnight. After decomposition of the intermediate compound the product was light yellow and after 3 recrystallizations from methyl alcohol melted at 134.5°; yield of crude material, 52%. The substance is soluble in benzene, acetone, ether, chloroform or acetic acid but only slightly soluble in methyl or ethyl alcohol. The product obtained by Conant and Lutz melted at 148°.

Di-p-toluyl-dibromo-ethane.—Two g. of the ditoluyl-ethylene was dissolved in 100 cc. of acetic acid and bromine slowly added. The bromine was immediately absorbed and colorless, needle-shaped crystals appeared; m. p., 200–200.5°. These were insoluble in benzene, toluene, ether or acetone, slightly soluble in acetic acid and more soluble in chloroform.

Analysis. Calc. for C₁₈H₁₆O₂Br₂: Br, 37.7. Found: 37 25.

Identification of Di-p-toluyl-dibromo-ethane.—One g. of the bromine addition compound was fused with 2 g. of potassium hydroxide for 10 minutes at 130°. The product on acidification gave p-toluic acid. This also identifies the di-toluyl-ethylene as di-p-toluyl-ethylene.

Di-p-toluyl-ethylene (cis).—Two g. of the trans compound was dissolved in acetic acid and allowed to remain in the sunlight for 3 days. At the end of this time some colorless crystals had appeared in the solution and more were obtained by evaporation of the solution; m. p., 148.5°. When the substance was recrystallized from ethyl alcohol the melting point became 152°. In acetic acid solution this product absorbed bromine and gave colorless needles identical with the bromine addition compound of the original compound. When the substance, m. p. 134.5°, was dissolved in acetone and exposed to sunlight for 2 days the product after one recrystallization melted at 147°. Further exposure to brighter sunlight for 2 days gave a small quantity of a substance melting at 120°. Conant and Lutz obtained the cis compound, m. p. 123°, and this is probably identical with my last product as I had not enough material for recrystallization.

Di-2,4-xylyl-ethylene (trans).—Seven g. of fumaryl chloride, 45 cc. of m-xylene, and 20 g. of aluminum chloride were used and the reaction proceeded at room temperature for several hours. After decomposition of the intermediate compound an oil was obtained, but on solution in methyl alcohol and gradual evaporation of the alcohol a yellow solid separated which on recrystallization from ethyl alcohol melted at 125.5-126°. It is quite soluble in benzene, acetone, ether, chloroform or acetic acid and slightly soluble in methyl or ethyl alcohol; yield, 15%.

Di-2,4-xylyl-dibromo-ethane.—Two g. of the dixylyl-ethylene was dissolved in 150 cc. of hot acetic acid and bromine gradually added. White needles formed; m. p., 145°. This product is insoluble in benzene, acetone or ether and slightly soluble in chloroform.

Analysis. Calc. for C20H20O2Br2: Br, 35.36. Found: 35.38.

acid containing reducing agents such as sulfur dioxide. It decomposes hydrogen peroxide without itself being changed. It oxidizes alcohols to the corresponding aldehydes.

- 4. It has been shown that the nitrates of lithium, potassium, calcium, barium and strontium are not nearly so satisfactory for the fusion with chloroplatinic acid as sodium nitrate.
- 5. A comparison of the catalytic activity of this oxide with the various oxides obtained by methods described in the literature has shown the former to be far superior. Moreover, it is much more readily prepared.

URBANA, ILLINOIS

[Contribution from the Chemical Warfare Service¹ and the Bureau of Chemistry, United States Department of Agriculture]

THE CONSTITUTION OF CAPSAICIN, THE PUNGENT PRINCIPLE OF CAPSICUM. III

By E. K. Nelson and L. E. Dawson Received July 2, 1923

In former contributions by one of us² capsaicin was shown to be the vanillyl amide of a decenic (decylenic) acid. Beyond proof that this decenic acid is not a straight-chain acid, its constitution remained undetermined. The primary purpose of the present work was to determine the structure of this acid, thereby establishing the complete structure of capsaicin.

On account of the scarcity of material at the time, it was decided to attack the problem from the synthetic end, which required, of course, the synthesis of a considerable number of 10-carbon acids. In order to simplify the work, the question of the location of the double bond was deferred for the time being, and a saturated acid was sought which, when condensed with vanillyl amine, would give a product identical with that obtained on hydrogenating the side chain of capsaicin.

Such an acid was finally found in 8-methyl-nonoic acid, which has been described by Levene and Allen.³

The location of the double bond in the decenic acid from capsaicin was finally determined by its oxidation with a 5% solution of potassium permanganate, the products being adipic acid and *iso*butyric acid.

This shows that the double bond is located between the sixth and seventh carbon atoms, and that capsaicin is the vanilly amide of Δ^6 , 8-methylnonenic acid,

$$\begin{array}{c} OCH_3 \\ HO \\ \hline \end{array} CH_2NHCO(CH_2)_4CH = CHCH(CH_3)_2 \end{array}$$

¹ Released by Chemical Warfare Service.

² Nelson, This Journal, 41, 1115 (1919); 42, 598 (1920).

³ Levene and Allen, J. Biol. Chem., 27, 433 (1916).

Experimental Part

Hydrogenated Capsaicin.—One g. of capsaicin, dissolved in absolute alcohol, when shaken in the presence of hydrogen with 0.05 g. of colloidal palladium, absorbed 2 atomic proportions of hydrogen within 10 hours. The product, recrystallized from petroleum ether, melted at 65°. Its solution in chloroform did not decolorize a dilute solution of bromine in the same solvent, whereas a solution of capsaicin immediately decolorizes bromine. The appearance and optical properties of hydrogenated capsaicin are very similar to those of capsaicin. The refractive indices, $n_{\rm D}^{20°}$ of the two compounds determined by the immersion method in potassium mercuric iodide solution were as follows.

	α	β	γ
Capsaicin	1.520	1.540	1.580
Hydrogenated capsaicin	1.510	1.520	1.555

In a second experiment, 0.6855 g. of the saturated acid, made by hydrogenating the decenic acid from capsaicin, was converted into the chloride and then condensed with vanillyl amine. The resulting product had the same physical and optical properties as the hydrogenated capsaicin and did not show unsaturation with very dilute solution of bromine.

Synthesis of 8-Methyl-nonoic Acid.—Ethyl isocaproate (110 g.) was reduced to 4-methyl-pentyl alcohol by the method of Levene and Allen.³ The yield of 4-methyl-pentyl alcohol, boiling at 150–152°, amounted to 52.3 g., or 67.3% of the calculated amount. This 4-methyl-pentyl alcohol (52.3 g.) was refluxed for 3 hours with 4 molecular proportions of hydriodic acid (b. p., 127°) and the resulting iodide was separated and rectified. A yield of 97.8 g. (90%) of 4-methyl-pentyl iodide was obtained. The 4-methyl-pentyl iodide was then condensed with aceto-acetic ester according to the method of Locquin,⁵ yielding 83 g. of 4-methyl-pentyl aceto-acetic ester, boiling at 155–160° (20 mm.).

The 4-methyl-pentyl aceto-acetic ester (83 g.) was saponified by the method of Dieckmann, which consisted in boiling it for 4 hours with 10 g. of sodium dissolved in 250 cc. of absolute alcohol. The resulting ethyl 6-methyl-heptylate, boiling at 201–203°, was obtained in a yield of 66.2%. At this point some unchanged material from previous operations was recovered and converted into ethyl 6-methyl-heptylate.

Ethyl 6-methyl-heptylate was reduced by the Levene-Allen method and 33.9 g. of 6-methyl-heptyl alcohol, boiling at 185–190°, was obtained. The corresponding iodide was prepared, with a yield of 56.3 g., boiling at 100–105° (17 mm.). This was condensed with aceto-acetic ester, affording ethyl 8-methyl-nonoate which, on being saponified, gave a yield of 27.4 g. of 8-methyl-nonoic acid, boiling at 150° (15–16 mm.).

Preparation of 8-Methyl-nonoyl Vanillyl Amide, OCH3

HO CH₂.NH.CO(CH₂)₆.CH(CH₃)₂.—The 8-methyl-nonoic acid (1.18 g.) was converted into the acid chloride, and the latter condensed with vanillyl amine. The 8-methyl-nonoyl vanillyl amide formed melted at 65° and a mixture with hydrogenated capsaicin gave no depression in melting point. Its optical properties were also identical with those of hydrogenated capsaicin.

The pungency of the synthetic product, as well as that of hydrogenated capsaicin, was proved by direct quantitative experiment to be as great

⁴ The optical measurements were kindly made by Dr. Edgar T. Wherry of the Bureau of Chemistry.

Locquin, Bull. soc. chim., [3] 31, 757 (1904).
 Dieckmann, Ber., 33, 2670 (1900).

as the pungency of capsaicin. This shows that the double bond exerts little or no influence on pungency, which is contrary to the assumption of Ott and Zimmermann⁷ that unsaturation in the side chain of capsaicin and related compounds is necessary for pungency. The preparation of the vanillyl amides of other synthetic saturated and unsaturated acids, the description of which is reserved for a later communication, has also disproved the assumption that unsaturation in the side chain is a requirement of pungency.

Oxidation of the Decenic Acid from Capsaicin.—The acid isolated from the capsaicin by heating it to 180° with a 25% solution of sodium hydroxide was oxidized in the cold with a 5% solution of potassium permanganate. A partially crystalline product was thus obtained. This was separated by distillation with steam into a non-volatile, crystalline acid and a volatile, liquid acid.

The crystalline acid melted at $147-150^{\circ}$ (adipic acid melts at $149-149.5^{\circ}$). 0.1703 g. of the silver salt yielded 0.1017 g. of silver, or 59.7%; calculated for silver adipate, 59.96%.

The volatile, liquid acid was also converted into the silver salt which was found to contain 54.99% of silver; calculated for silver *iso*butyrate, 55.34%. This was known to be *iso*butyric acid on account of our knowledge of the structure of the corresponding saturated acid. The decenic acid from capsaicin is thus shown to have the double bond between the sixth and seventh carbon atoms and is therefore Δ^6 , 8-methyl-nonenic acid.

Summary

Hydrogenated capsaicin has been prepared and found to be very similar to capsaicin in all its properties, except that it does not decolorize a dil. bromine solution and differs in the refractive indices of its crystals.

A compound identical in all respects with hydrogenated capsaicin was prepared by condensing 8-methyl-nonoic acid with vanillyl amine.

A study of this compound has shown that it is quite as pungent as capsaicin and that the double bond is not necessary for pungency.

The unsaturated acid from capsaicin has been found to have its double bond in the 6 position, thus showing that capsaicin is Δ^6 , 8-methyl-nonenyl vanillyl amide.

WASHINGTON, D. C.

⁷ Ott and Zimmermann, Ann., 425, 314 (1921).

[Contribution from the Department of Pharmacology, Harvard Medical School,]

SOME DERIVATIVES OF ARSPHENAMINE¹

By Walter G. Christiansen

Received July 9, 1923

The Preparation of Arsphenamine Polyarsenide

In a previous communication from this Laboratory,² the preparation of arsphenamine polyarsenides by reduction of a mixture of 3-amino-4-hydroxyphenylarsenious oxide and sodium arsenite with hypophosphorous acid is described. The arsenic content of the product varies from 47.3 to 53.7% depending upon the ratio of the organic arsenical to the sodium arsenite prior to the reduction. In spite of the fact that these specimens contain $^2/_3$ as much arsenic again as arsphenamine, they are tolerated in doses as large as 140 mg./kg.; many samples of arsphenamine are not tolerated at this dose.

It was shown³ that the toxicity of aromatic amino arseno compounds in general, when prepared from nitro aryl arsonic acids by reduction with sodium hydrosulfite, can be made to vary considerably depending upon the conditions under which the nitro group is reduced, and two sets of conditions for reduction of the nitro group have been developed so that, while using the same quantities of all reagents in both cases, the arsphenamine will be tolerated (a) in fairly large doses and (b) in only rather small doses.4 An investigation of the sulfur compounds in arsphenamine evinced that the more toxic samples prepared by improper reduction of the nitro group contain approximately 2% of sulfur, whereas when the most favorable conditions are employed the sulfur content is only 0.8%.5 A more recent study⁶ proved that when a certain amount of acetic acid is present while 3-nitro-4-hydroxyphenylarsonic acid is being reduced under the most favorable conditions by commercial hydrosulfite to arsphenamine base, the yield is increased without any alteration in the toxicity, but that when too much acid is employed the toxicity of the product suddenly increases.

A study of the production of arsphenamine polyarsenide by reduction of 3-nitro-4-hydroxyphenylarsonic acid and sodium arsenite with sodium

¹ This is the 13th of a series of studies on the properties contributing to the toxicity of arsphenamine being made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School; the work is under the general direction of Doctor Reid Hunt.

² Christiansen, This Journal, 43, 373 (1921).

³ Christiansen, ibid., 43, 2202 (1921).

⁴ Ref. 3, p. 2207.

⁵ Christiansen, This Journal, 44, 848 (1922).

⁶ Christiansen, *ibid.*, **45**, 1319 (1923).

hydrosulfite shows clearly that the relations found between the mode of synthesis and the toxicity of arsphenamine as summarized above hold true in this case also. Tabulation of the results brings out the differences very distinctly.

Table I
The Relation between the Mode of Synthesis and the Toxicity of Arsphenamine
Polyarsenide

Substances reduced	Reducing agent	Expt.	Tol. dose Mg./kg.	As content %	S conte nt %
3-Amino - 4 - hydroxy-phenylarseni-			140	50.81	
ous oxide and sodium arsenite2	$\mathrm{H_3PO_2}$	3	140	47.31	
			140	53.72	
3 - Nitro - 4-hydroxy - phenylarsonic					
acid and sodium arsenite	$Na_2S_2O_4$ (a)	2	∫ 120	44.76	
			120	43.76	1.78.
	(b)	1	80	41.87	2.38
	(c)	1	<80	45.55	

- (a) The nitro group was reduced under the most favorable conditions.
- (b) The nitro group was reduced under the least favorable conditions.
- (c) An excess of acetic acid was present during the reduction.

The arsenic determinations show that the composition of arsphenamine polyarsenide is very variable, and the substance may be best represented

by the formula
$$\begin{pmatrix} -As = As - \\ NH_2 \cdot HC1 \end{pmatrix} As_n$$
. When $n = 2$ the $\begin{pmatrix} NH_2 \cdot HC1 \\ OH \end{pmatrix}$

calculated arsenic content is 50.9%. One of the factors controlling n is the ratio between the quantities of arsonic acid and the sodium arsenite used.

Experimental Part

A. To a vigorously stirred, cold (8°) solution of 10.6 g. of magnesium chloride hexahydrate in 260 cc. of water, 50 g. of sodium hydrosulfite is added, and after about 30 seconds a cold (8°) solution of 2 g. of 3-nitro-4-hydroxyphenylarsonic acid in 46 cc. of water containing 0.66 g. of sodium hydroxide is added gradually during 1 to 1.5 minutes. Two g. of decolorizing carbon is added, and the material, after being heated rapidly to 30°, is filtered. A solution of 0.9 g. of arsenious oxide in 45 cc. of water containing 0.37 g. of sodium hydroxide is added to the clear filtrate, and the solution is heated rapidly with stirring to 55° and maintained at 55–60° for 90 minutes. The arseno compound separates as a finely divided, brownish-yellow solid. The base is removed by filtration and, after it is washed and dried in a vacuum over sodium hydroxide, is converted into the dihydrochloride by dissolving it in 10.5 cc. of absolute methyl alcohol containing a slight excess over 2 moles of dry hydrogen chloride. Filtration will not remove some of the very finely divided insoluble matter, but centrifuging for 5 or 10 minutes produces a clear, bright red alcoholic solution which is poured into 110 cc. of ether previously cooled to 0–5°. After this is filtered, washed with ether and dried in a vacuum over sodium

hydroxide, 1.4 g. of a reddish-orange arsphenamine polyarsenide is obtained which dissolves very readily in water forming a clear, deep red solution. The product is tolerated in doses of 120 mg./kg. and contains 44.2% of arsenic (the average of 2 experiments) and 1.78% of sulfur.

An aqueous solution of the polyarsenide is slightly acid to litmus, gives an orange-colored precipitate of the sulfate when treated with sodium sulfate, and an orange-colored precipitate of the free base when sodium acetate or carbonate is added; these precipitates redissolve in sodium hydroxide forming clear, red solutions. When the aqueous solution is added to coned. hydrochloric acid or to acetone, the dihydrochloride is reprecipitated. When iodine is added to the red aqueous solution, the material is oxidized and the red color is destroyed. In alkaline solution, the compound is oxidized by hydrogen peroxide and the red color disappears.

- B. All of the reagents are used in the same quantities as in A. The dilute, warm (30°) aqueous magnesium chloride solution is stirred very slowly, and immediately after the hydrosulfite has been added, the warm (30°) nitro solution is added very rapidly (5 seconds). The solution is stirred rapidly for about 1 minute to dissolve the remainder of the hydrosulfite completely and then is filtered. The arsenite solution is added, and after the mixture is heated slowly to 55° and stirred vigorously the experiment is continued as in A; yield, 1.4 g. of reddish-orange polyarsenide which dissolves very readily in water to give a clear, red solution. The product is tolerated in doses of only 80 mg./kg. and contains 41.87% of arsenic and 2.38% of sulfur.
- C. This experiment is conducted as described in A, but after the arsenite solution has been added 4 cc. of glacial acetic acid is added; yield, 1.5 g. of reddish-orange polyarsenide which is very readily soluble in water, forming a clear, red solution and which contains 45.55% of arsenic. It is not tolerated in doses of 80 mg./kg.

The toxicity determinations were made by injecting 2% alkalinized solutions intravenously into albino rats. The solutions were prepared by adding 4 molecular equivalents of N sodium hydroxide solution to an aqueous solution of the dihydrochloride.

Sulfarsphenamine

Recently the production of sulfarsphenamine, a compound similar to neo-arsphenamine, has been described and, owing to its low toxicity, therapeutic efficiency, stability in aqueous solution and the fact that it can be injected subcutaneously, it may become quite important in the treatment of syphilis. Voegtlin and Johnson prepared this substance by condensing arsphenamine with 2 molecular equivalents of formaldehyde and adding 4 equivalents of sodium bisulfite to the condensation product; the following formula has been assigned to it.

molecular equivalents of the aldehyde and bisulfite, respectively, were used. When an attempt was made to prepare this substance by following Voegtlin and Johnson's directions, using 2 moles of formaldehyde and 4 moles of bisulfite per mole of arsphenamine, the precipitate formed by the addition of bisulfite redissolved only partially; consequently, the yield

Voegtlin and Johnson, This Journal, 44, 2573 (1922).

was very low. This was found to be due to incomplete condensation between the arsphenamine and the formaldehyde. However, when 3 moles, that is 50% excess of the aldehyde are used, the initial precipitate redissolves completely when only 2 moles of bisulfite have been added. The reaction product which is isolated when 3 moles of aldehyde and 2 moles of bisulfite are employed is not tolerated in doses above 250 mg./kg. and contains less than 1 sulfur atom per atom of arsenic; in this case complete reaction has not been obtained between the bisulfite and the formaldehyde condensation product. By adding another mole of bisulfite after the initial precipitate has redissolved complete reaction is obtained, and the product is tolerated in doses of 350-400 mg./kg. It seems that 3 moles of formaldehyde and 3 moles of bisulfite are much more favorable than 2 and 4 moles, respectively, and the use of bisulfite in excess of the necessary amount, namely, 3 moles, increases the opportunity for contamination of the product with bisulfite and does not improve the product in any noticeable way.

Voegtlin and Johnson lay great stress upon the quality of the bisulfite and state that it must be pure and freshly prepared from sodium carbonate and sulfur dioxide. This is entirely unnecessary and the sulfarsphenamine made from the purified sodium bisulfite which is on the market is the equal in every respect of that secured by the use of freshly prepared, pure bisulfite.

Moreover, it is unnecessary to prepare arsphenamine, that is, the dihydrochloride, to start with. When the dried base obtained by the reduction of 3-nitro-4-hydroxyphenylarsonic acid with sodium hydrosulfite is dissolved in water by the addition of a small amount of hydrochloric acid, this solution serves just as well as one prepared from the dihydrochloride itself.

These two changes, namely, the use of commercial bisulfite and of arsphenamine base instead of the purified dihydrochloride, simplify the production of sulfarsphenamine and lower the cost of its preparation considerably.

Also, sulfarsphenamine that will be tolerated in doses of 350–400 mg./kg. can be prepared from toxic arsphenamine, that is, arsphenamine that is not tolerated at 70 mg./kg., and which was prepared by improper reduction³ of the nitrohydroxy acid.

In Table II, the results of a series of experiments are recorded on which the above conclusions are based. Three molecular equivalents of formaldehyde were used in each experiment.

When the comparatively toxic arsphenamine that has been secured by improper reduction of the nitro acid with hydrosulfite is converted into sulfarsphenamine, the initial precipitate formed by the addition of the bisulfite after the condensation with formaldehyde redissolves in less than 40 seconds, which is very much more rapidly than when relatively non-toxic arsphenamine is used. Since the arsphenamine in this case contains about 2% of sulfur, most of which is present as a sulfonic acid derivative of arsphenamine, it is to be expected that the resulting sulf-

Table II
THE PREPARATION OF SULFARSPHENAMINE

		Sulfarsphenamine				
Arsphenamine Tol. dose about	NaHSO ₄ Mol.	$_{\%}^{\mathrm{As}}$	S %	As:S	Tol. dose Mg./kg.	
100	2^a	24.48	8.89	1:0.85	<250	
100	$1. 2^{b}$	25.11	9.34	1:0.87	250	
100	$ 2^{b}$	24.75	9.48	1:0.901	250	
100	3^{b}	21.83	10.96	1:1.17	400 or above	
100	$\dots 3^b$	21.99	11.10	1:1.18	400	
100	$\dots 4^b$	20.80	11.13	1:1.26	350	
140 or above e	· · ·	21.55	11.16	1:1.21	400	
$70^{\circ}\dots$	$ \int 3^b$	19.36	10.97	1:1:33	350-400	
Arsphenamine base ^d	$\dots 3^b$	21.55	11.16	1:1.21	400	

^a Freshly prepared, pure bisulfite.

arsphenamine would have a larger ratio of sulfur to arsenic than when the original material contains little sulfur.

Since sulfarsphenamine should contain 25.1% of arsenic, the material obtained by these reactions is only about 87% pure. To determine the effect, if any, that the impurities have on the toxicity, some of the crude sulfarsphenamine which was tolerated at 350 mg./kg. was converted into the free acid by treatment with acetic acid. The dry, purified acid was reconverted into the sodium salt by solution in the calculated quantity of sodium carbonate and precipitation with alcohol. The sodium salt then contained 25.9% of arsenic and was tolerated in doses of 300-350 mg./kg. Therefore, the impurities in crude sulfarsphenamine are comparatively inert and have little bearing on the toxicity of the substance.

Experimental Part⁸

A. Two and one-half g. of arsphenamine is moistened with 4 cc. of alcohol, dissolved in 32 cc. of water with the aid of mechanical stirring, and 1.25 cc. of formalin (about 37% formaldehyde) is added. After 1 minute, 3.3 cc. of a solution of commercial sodium bisulfite (3.7 g. of bisulfite in 10 cc. of solution) is added; the precipitate that forms gradually redissolves, and after 10 minutes 1.6 cc. more of the bisulfite solution is added. The stirring is continued for 20 minutes, and then, after filtration, the clear, orange-yellow solution is poured into 5 volumes of alcohol. The sulfarsphenamine is separated,

^b Commercial, pure bisulfite.

^c The arsphenamine was prepared by improper reduction of the nitro acid with hydrosulfite.

^d This base is the same as that from which e was prepared.

^e Compare d, above.

⁸ The experimental procedure is, in general, that reported by Voegtlin and Johnson⁷ but owing to the changes in quantities and time, which seem advisable as a result of experiments in this Laboratory, the entire process is outlined again for the sake of clarity.

washed with 95% alcohol and absolute alcohol, and dried in a vacuum over sodium hydroxide; yield, 3 g. of sulfarsphenamine that is very readily soluble in water, forming a clear, orange-yellow solution; it contains arsenic and sulfur in the ratio of 1:1.19. The product is tolerated in doses of 400 mg./kg.

B. A suspension of 2.1 g. of arsphenamine base in 32 cc. of water is stirred mechanically and treated with 0.9 cc. of concd. hydrochloric acid (approximately 2 moles). As soon as the base has dissolved completely, the experiment is continued as in A. In this case the solution commences to become viscous about 30 seconds after the aldehyde has been added, whereas in A this never occurs in less than 1 minute. The bisulfite is added as soon as marked signs of viscousness appear. Three g. of cream-colored sulfarsphenamine is obtained, which dissolves readily in water forming a clear, deep yellow solution and which contains arsenic and sulfur in the ratio of 1:1.21. The product is tolerated in doses of 400 mg./kg.

The toxicity of these preparations was determined by intravenous injection of 6% solutions into albino rats.

During large scale work in the Arsphenamine Laboratory of the Massachusetts State Health Department, the same trouble was encountered as in this Laboratory in obtaining satisfactory results with the quantities recommended by Voegtlin and Johnson. Since the adoption of the changes in quantities herein recommended, these difficulties have been avoided. Also, comparatively large quantities of sulfarsphenamine have been prepared from toxic and non-toxic arsphenamine using commercial bisulfite and the product was tolerated in doses of 400 mg./kg.

A Polyarsenide of Sulfarsphenamine

When arsphenamine polyarsenide is subjected to the procedure used in preparing sulfarsphenamine, a very soluble sodium salt is obtained which may be called sulfarsphenamine polyarsenide. When the bisulfite is added, after the arsphenamine polyarsenide has been condensed with formaldehyde, an orange-colored precipitate forms that redissolves very quickly. The dried sodium salt is an orange-colored powder that dissolves in water forming a deep red solution. Although the toxicity of arsphenamine polyarsenide differs very little from that of arsphenamine, the polyarsenide of sulfarsphenamine is not tolerated in doses even as low as 200 mg./kg., whereas sulfarsphenamine itself is tolerated at 400 mg./kg.

Summary

Arsphenamine polyarsenide may be obtained by reduction of 3-nitro-4-hydroxyphenylarsonic acid and sodium arsenite with sodium hydrosulfite, and the toxicity of the product depends on the mode of reduction just as does that of arsphenamine. In spite of its high arsenic content as compared with arsphenamine, its toxicity differs but little from that of the latter substance.

By modifying the quantities of reagents certain difficulties encountered while preparing sulfarsphenamine by the original method have been overcome. It is unnecessary to use freshly prepared, pure sodium bisulfite in this reaction; commercial bisulfite suffices. Also, it is unnecessary to start with arsphenamine, that is, the dihydrochloride; equally good results can be secured by starting with dry arsphenamine base.

As the impurities present in the crude sulfarsphenamine have little bearing on the toxicity, it is unnecessary to purify the material.

Arsphenamine polyarsenide can be converted into a polyarsenide of sulfarsphenamine, but this substance is comparatively toxic.

Boston 17, Massachusetts

[Contribution from the Department of Pharmacology, Harvard Medical School]

THE ARSONATION OF PHENOL¹

By Walter G. Christiansen and Arthur J. Norton Received July 9, 1923

In synthesizing arsphenamine from aniline or phenol by any of the common methods,² all of the reactions except that in which the arsenical group is introduced into the benzene nucleus progress smoothly, and excellent yields (75% or over) are easily obtained. Owing to the low yields obtained when aniline or phenol is arsonated with arsenic acid, the cost of production of the final product is greatly influenced by this reaction. Cheetham and Schmidt,³ by modifying the conditions for arsonating aniline, secured recrystallized arsanilic acid in 26% yields, whereas the yields obtained by previous methods averaged approximately 15%. The arsonation of phenol with arsenic acid has been discussed in two papers; one by Conant⁴ and the other by Jacobs and Heidelberger,⁵ and in both cases the yield of hydrated sodium p-hydroxyphenylarsonate is given as approximately 20%. Conant suggests that by proper adjustment of the experimental conditions, it should be possible to raise the yield to about 30%.

For the production of sodium p-hydroxyphenylarsonate in this Laboratory, the method of Jacobs and Heidelberger was adopted but the yield averaged only 18% instead of 20. The main reaction is expressed by the equation

¹ This investigation was undertaken in connection with a study of arsphenamine which was made under a grant from the United States Interdepartmental Social Hygiene Board to the Harvard Medical School; the work was under the general direction of Dr. Reid Hunt.

² For a brief outline of these methods see Lythgoe, Chem. Age, 28, 390 (1920).

³ Cheetham and Schmidt, This Journal, 42, 828 (1920).

⁴ Conant, ibid., 41, 431 (1919).

⁵ Jacobs and Heidelberger, ibid., 41, 1440 (1919).

By systematic modification of the reaction conditions the yield has gradually been raised until it is now possible to secure the product in 33% yields; although this is not a high yield, it is a very distinct improvement over an 18--20% yield.

Jacobs and Heidelberger mix sirupy arsenic acid (from which the excess of water has been removed by boiling to 150°) with phenol in a flask and heat the mixture under a reflux air condenser in an oil bath maintained at 155-160° for 7 hours. At first the substances remain as 2 distinct layers and the temperature inside the flask is approximately 145°, but as the reaction progresses the contents of the flask become homogeneous and the temperature falls steadily to about 130° due to the retention of the water eliminated by the reaction. Inasmuch as the reaction takes place, for some time at least, between 2 distinct phases, it seems advisable to stir the reacting materials as efficiently as possible. Also, the temperature of the reaction mixture should not be permitted to decrease to any great extent as it is accompanied by a marked decrease in the speed of reaction. This can be avoided by letting the water which is formed distil during the first part of the reaction. Since p-hydroxyphenylarsonic acid is hydrolyzed in water to a marked degree even at 130°6 there is a tendency for the reverse of Reaction 1 to take place and it should probably be written as a reversible reaction. Owing, however, to the excess of arsenic acid and comparatively small amount of water the equilibrium would be far to the right. If the water is allowed to escape, the tendency toward reversal of the reaction will be diminished and the yield should be increased. Thus, to show clearly the extent to which water affects the reaction, when 200 g. of boiled arsenic acid, 100 g. of phenol and 20 cc. of water are heated and stirred under sufficient pressure to maintain the mixture at 140-150°, no reaction takes place.

All the detailed experiments that were made while the individual experimental conditions were being examined will be omitted in this report and only the method finally adopted will be carefully described.

Experimental Part

Three hundred and sixty g. of sirupy arsenic acid (75–80%) is boiled in a beaker until the temperature of the acid is 150°; about 60 g. of water is driven off leaving a sirup containing approximately 95% of orthoarsenic acid which is then added to 150 g. of phenol in a 500cc. round-bottom short-neck flask. By means of a 3-hole stopper, an efficient, jacketed stirrer and a thermometer are introduced into the flask and a connection is established with a downward condenser. The flask is set in an oil-bath which is heated at once to 155–160°, and the stirrer is run at a rate high enough to insure thorough mixing of the contents of the flask. When the inside temperature reaches 140° boiling commences, and water plus a very little phenol begins to distil. The distillation is allowed to continue until 30 cc. (1 molecular equivalent) of water has been collected; this usually requires 1 to 1.5 hours, and the inside temperature rises to 146°. The downward

⁶ Schmitz, Ber., 47, 370 (1914).

condenser is then replaced by a return air condenser, and the reaction is allowed to continue until a total of 7 hours has elapsed from the time the contents of the flask first reached 140°. After the return condenser has been attached, the inside temperature declines slowly to 141° or 142°, and the reaction mixture becomes thicker and somewhat tarry. After the contents of the flask have been partially cooled, they are poured into 2 liters of water and mechanically stirred; the agitation is continued for a short time in order to break up the tarry material and enable the water to dissolve the hydroxyphenyl arsonic acids completely.

The reaction mixture is worked up by the method employed by Jacobs and Heidelberger, with a few modifications. Finely ground, fresh barium hydroxide is added gradually to the well-stirred water solution until the material is slightly alkaline to litmus, in order to remove the excess of arsenic acid; when this point is reached the solution becomes pink. If the procedure is carried out properly, 350-400 g. of Ba(OH)₂.8H₂O should suffice. The time required by this method is greater than when a hot solution of barium hydroxide is used, but the method is more convenient and does not cause such a great increase in volume. After removal of the barium arsenate, by filtration, the mother liquor and washings are treated with sulfuric acid until the solution contains neither barium nor sulfate ions. When the barium sulfate has been separated and thoroughly washed, the filtrate is concentrated on a steam-bath to about 1.5 liters, neutralized to litmus with sodium hydroxide, filtered, evaporated until the solution becomes well coated with crystals and then treated with 2.5 volumes of alcohol. After the mixture has cooled in an ice box the sodium p-hydroxyphenylarsonate is separated, washed with alcohol and dried in an oven at 80°. A second crop may be secured from the filtrate by concentrating it further and precipitating with alcohol. The total yield of anhydrous sodium p-hydroxyphenylarsonate is 126 g. (33%). By proper manipulation it is possible to obtain as much as 122 g. in the first crop and to have it free from sulfate, arsenate and sodium o-hydroxyphenylarsonate, which is one of the by-products formed in this reaction.⁵

When the downward condenser is not replaced by a return condenser, the total volume of water that distils is 55-60 cc., whereas the arsonation of phenol should liberate only 1 molecular equivalent (30 cc.) of water. Moreover, when all of the water is removed from the reaction chamber in this way, the mass becomes very tarry; the tar formation was so extensive in one experiment that the reaction had to be discontinued after 5.5 hours. The oxidation of organic matter to tarry material by the arsenic acid is the source of the excess of water that distils. To determine whether the reaction product is destructively oxidized, 20 g. of anhydrous sodium p-hydroxyphenylarsonate and 57 g. of boiled arsenic acid were heated and stirred so that the inside temperature was 145-150° for 3.5 hours. During this time, no water distilled, there was not the slightest trace of tar formation, and 15 g. of pure, anhydrous sodium p-hydroxyphenylarsonate was recovered from the material by working as described above. As there are slight, unavoidable mechanical losses incident to the use of the long process required to isolate the product, and as the original material was not exceptionally pure, the recovery of 15 g. is very good. This experiment proves conclusively that the reaction product is not destroyed when subjected to the action of hot arsenic acid and that the tar must be formed either from phenol that has not been acted on or from an intermediate substance formed in the reaction.

⁷ Carefully washed barium arsenate proved just as efficient as lead arsenate as an insecticide when sprayed on potato plants and, when suspended in water, could be used in a spraying machine without difficulty.

⁸ The filtration of large quantities of barium sulfate is usually tedious, but if filtering carbon is added to the suspension to be filtered and if a mat of this carbon is prepared on the filter by filtering an aqueous suspension of carbon, the barium sulfate may be removed rapidly and completely even when it is precipitated from cold solutions.

possible that the first step in the reaction is the formation of a phenyl ester of arsenic acid analogous to the known phenyl esters of sulfuric and phosphoric acids^{9,10,11} and that this then rearranges to the p- and o-hydroxyphenylarsonic acids.

It has been frequently noted that the second crops of sodium p-hydroxy-phenylarsonate contain some material insoluble in water and that the amount of this material varies directly with the degree of tar formation during the reaction. Examination of the insoluble matter showed that it is chiefly arsenious oxide which must be formed when the arsenic acid acts as an oxidizing agent. A few catalysts, such as copper arsenate, iodine or a dehydrated clay, were introduced but in each case the yield decreased instead of increased. It was hoped that the finely divided, dehydrated clay would provide a surface on which the two liquids might react and would facilitate the removal of water.

As Jacobs and Heidelberger⁵ state that, after the removal of the barium sulfate, it is preferable to concentrate the solution in a vacuum, it seemed advisable to determine the extent to which the product is hydrolyzed in boiling water.

This was done by distilling 100 cc. of a 5% aqueous solution with steam so that 20 cc. of distillate collected every 5 minutes and analyzing the distillate for phenol by the bromine method, that is, by addition of an excess of bromine water of known strength, the determination of the excess of bromine by the addition of potassium iodide and titration of the liberated iodine with thiosulfate solution. When solutions of pure phydroxyphenylarsonic acid prepared either from the acid itself or by addition of hydrochloric acid to a solution of the purified sodium salt are examined in this way, the distillate is found to contain only 0.1 to 0.5 mg, of phenol in each 20 cc. After a slight excess of sodium carbonate has been added to the solution being distilled, the phenol content of the distillate is found to be approximately 1.0 mg. in 20 cc. The steam-distilled solution gives a very slight reaction for arsenic acid when tested with hydrogen sulfide. When 250 cc. of a 0.5% solution of phenol in water is distilled with steam, the distillate at first contains 156 mg, in each 20 cc, and it is only after prolonged distillation, namely, when the concentration of the phenol solution has become very low that the distillate contains only 1 mg. of phenol in 20 cc. Consequently, the hydrolysis of p-hydroxyphenylarsonic acid and its sodium salt is practically nil at 100°. This agrees with Schmitz'12 conclusion which was arrived at by another method. These results indicate clearly the absence of any necessity for concentrating the solutions in a vacuum.

The modifications of Jacobs and Heidelberger's method of arsonating phenol outlined in this paper have been applied to large-scale production in the Arsphenamine Laboratory of the Massachusetts State Department

- ⁹ Baumann, Ber., 11, 1907 (1878), isolated the phenyl ester of sulfuric acid as its potassium salt which, when heated, rearranged mainly to potassium p-phenolsulfonate. Similar results were obtained with other phenols.
- ¹⁰ Heymann and Koenigs, *ibid.*, **19**, 3304 (1886), obtained the potassium salt of phenylphosphoric acid.
- ¹¹ A phenyl ester of arsenious acid is known. Lang, Mackey, and Gortner, J. Chem. Soc., 93, 1364 (1908).
 - 12 Ref. 6, p. 368.

of Health, and the yields have increased very greatly over those that were obtained prior to the institution of these changes.

Summary

By vigorous agitation of the reacting substances and partial removal of the water produced during the arsonation of phenol by arsenic acid, it is possible to secure a 33% yield of anhydrous sodium p-hydroxyphenylarsonate instead of the 20% yield obtained by previous methods.

It is suggested that a phenyl ester of arsenic acid may be an intermediate in the formation of hydroxyphenylarsonic acids by this reaction.

By distillation of aqueous solutions of p-hydroxyphenylarsonic acid, with steam, it is shown that at 100° this substance hydrolyzes scarcely at all into phenol and arsenic acid. This confirms Schmitz' results obtained by another method.

BOSTON 17. MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, HARVARD MEDICAL SCHOOL]

N-METHYL-PARA-AMINO-ORTHO-CHLOROPHENOL SULFATE, A NEW PHOTOGRAPHIC DEVELOPER

By Walter G. Christiansen Received July 9, 1923

For a number of years N-methyl-p-aminophenol sulfate (Metol) has been the outstanding member of the aminophenol class of photographic developing agents, but analogous substances with additional groups attached to the benzene ring have not been investigated to determine the effect of these groups on the photographic developing properties of Metol. In this Laboratory the hydrochloride of p-amino-o-chlorophenol and the sulfate of its N-monomethyl derivative have been prepared. These compounds possess excellent developing properties when tested on both plates and paper but the methyl derivative is the superior; the finished plates and prints obtained by use of the latter substance are indistinguishable from those secured when Metol is used, but this material shows no marked advantages over Metol. Consequently, it may be concluded that the presence of a nuclear chlorine atom has little influence on the ability of Metol to function as a photographic developer. The amine is methylated by a well-known method, namely, condensation with formaldehyde and reduction of the condensation product.

Experimental Part

p-Nitro-o-chlorophenol. —A mixture of 10 g. of c. p. p-nitrophenol with 200 cc. of concd. hydrochloric acid is heated in a tall, narrow beaker until solution is complete.

¹ The method herein described is a modification of that used by Kollrepp, Ann., 234, 3 (1886).

The solution is cooled to room temperature while it is stirred mechanically, and the nitrophenol partly separates again in very fine crystals. A special type of stirrer is used, because during the last part of the reaction, that is, after chlorination, the mass in the beaker is a thick paste. The stirrer is constructed from an ordinary T stirrer with long arms by bending the ends of the arms into vertical positions so that they are close to the walls of the beaker. Through a long-stem dropping funnel, the end of which is in the acid and just above the horizontal section of the stirrer, a solution of 3 g. of potassium chlorate in 60 cc. of water is run in slowly while the mixture is vigorously stirred with this device. The nitrophenol dissolves and then the chloro compound starts to separate. As the reaction proceeds, the paste becomes very thick, but the vigorous stirring prevents the end of the dropping funnel from becoming plugged and permits the chlorate solution to run into the mixture. The agitation is continued for 1/2 hour and the mixture is allowed to stand overnight. After filtration, washing with water and air drying, 11 g. of nearly white p-nitro-o-chlorophenol melting at 106-8° is obtained: the pure compound melts at 110°.1

The product can be purified by suspending it in hot water and adding glacial acetic acid gradually until the material dissolves completely. As the solution cools, pure p-nitro-o-chlorophenol separates.

p-Amino-o-chlorophenol.—Sodium hydrosulfite (about 40 g.) is added gradually to a boiling solution of 10 g. of p-nitro-o-chlorophenol in 60 cc. of water containing 0.27 g. of sodium hydroxide, until the red color disappears. As the solution cools p-amino-o-chlorophenol precipitates. After this is separated, washed with water and air-dried, 5 g. of compound, m. p., 2 150–151°, is obtained as a white powder. By recrystallization from water, the substance can be secured in white needles.

Three g. of the amine is suspended in 25 cc. of water and treated with hydrochloric acid until it dissolves, and decolorizing carbon is added. The colorless solution obtained by filtering out the carbon is added to 35 cc. of coned. hydrochloric acid. After the liquid has been thoroughly cooled, the precipitated hydrochloride of p-amino-o-chlorophenol is separated, washed with hydrochloric acid and dried in a vacuum over sodium hydroxide. The white solid dissolves very readily in water to give a colorless solution that is acid to litmus but not to congo red. Ferric chloride oxidizes the material with the development of a deep blue color. When a solution of p-dimethylamino-benzaldehyde in dil. hydrochloric acid is added to an aqueous solution of the above hydrochloride, the solution becomes orange colored and an orange precipitate separates. In sodium hydroxide solution this amino chlorophenol oxidizes and becomes dark brown.

N-methyl-p-amino-o-chlorophenol.—A solution of 8.5 g. of p-nitro-o-chlorophenol in 200 cc. of water and 62.5 cc. of aqueous sodium hydroxide (d., 1.324) in a 500cc. round-bottom flask is heated to boiling. While it is being stirred mechanically, 20 g. of zinc dust is added during 10-15 minutes; this is sufficient to reduce the nitro group and produce a colorless solution. An additional 10 g. of zinc dust is added at once. A 3-hole stopper is inserted into the neck of the flask. Through 1 hole is a glass tube that dips below the liquid in the flask and serves as a sleeve for the stirrer, the second hole permits a reflux condenser to be attached and through the third hole a long-stem dropping funnel is introduced so that the end of the stem is below the surface of the liquid. The liquid is refluxed for 15 minutes and stirred vigorously, and then 5 cc. of formalin (37% formaldehyde) is added during 15 minutes. The refluxing is continued for 15 minutes longer and the solution is filtered through a hot funnel into a flask containing 10 g. of sodium bisulfite.³ Coned. hydrochloric acid (about 70 cc.) is added until the precipitate that

² Kollrepp obtained this compound by another method of reduction and found the melting point of the pure substance to be 153°. Ref. 1, p. 6.

³ The bisulfite prevents the hot alkaline solution from oxidizing and becoming black.

forms is redissolved, and then sodium carbonate is added until the solution no longer effervesces; this requires about 13 g. of sodium carbonate monohydrate. After the mixture has cooled it is extracted with three 50cc. portions of amyl acetate, and the extracts are filtered. By adding sulfuric acid dropwise to the amyl acetate, the amino compounds are precipitated as sulfates which are filtered out and extracted very thoroughly several times with alcohol to remove impurities. After it has dried, 7 g. of crude N-methyl-p-amino-o-chlorophenol sulfate is obtained.

By recrystallization from water, using decolorizing carbon, this substance separates as fine white needles that dissolve in water forming a colorless solution that is acid to litmus. The aqueous solution when treated (a) with ferric chloride becomes red and then very deep purple, (b) with sodium nitrite gives a white precipitate, (c) with sodium carbonate becomes brown.

Analyses. Calc. for $(C_7H_8ONCl)_2H_2SO_4.H_2O$: Cl, 16.45; S, 7.45. Found: Cl, 16.55, 16.25; S, 7.49, 7.45.

I wish to acknowledge the assistance of Mr. Arthur J. Norton in some of the experimental work.

Summary

The preparation of p-amino-o-chlorophenol hydrochloride and N-methyl-p-amino-o-chlorophenol sulfate is described. Both of these substances are good photographic developing agents but the methylated compound is the better. The latter compound appears to be equal to but no better than Metol, from which it differs only in having a chlorine atom attached to the benzene ring.

BOSTON 17, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, HARVARD UNIVERSITY]

REDUCTION POTENTIALS OF QUINONES. I. THE EFFECT OF THE SOLVENT ON THE POTENTIALS OF CERTAIN BENZOQUINONES

By James B. Conant and Louis F. Fieser Received July 11, 1923

The measurement of reduction potentials affords a new method of studying quantitatively the free energy of an addition reaction which can be brought about with a series of related substances. By such quantitative studies the differences caused by substitution and by structural changes can be discovered and when sufficient data have been obtained it should be possible to make many interesting and important generalizations in regard to the driving force of a given organic reaction and the structure of the organic compound concerned.

The normal reduction potential of a quinone is a measure of the free energy of the reduction of that quinone in the solvent employed. It has been found that the normal potential for certain benzoquinones in aqueous solution is affected by the presence of salt¹ and that the potentials of a

¹ S. P. L. Sörensen, M. Sörensen and Linderström-Lang, Ann. chim., 16, 283 (1921).

number of quinones in mixtures of alcohol and aqueous acid are somewhat different from the values obtained in aqueous solution.² This effect of the change of solvent on the potential is related to the ratio of the solubility of the quinone and hydroquinone as Sörensen has carefully proved. In the light of these results it is necessary to consider the following questions: to what extent are the reduction potentials of a series of organic compounds influenced by these solubility ratios and, further, in comparing the effects of substitution in quinones what solvent or solvents should be employed in measuring the potentials? To answer these questions we have determined the potentials of a series of benzoquinone derivatives (1) in alcoholic solution, (2) in aqueous solution and (3) under conditions in which the nature of the solvent does not influence the potential.

When we consider a cell composed of a hydrogen electrode immersed in a certain solvent connected with a half-cell containing an inert electrode immersed in the same solvent saturated with both the hydroquinone and quinone in question and containing both solid substances, it is obvious that on the passage of 2 faradays of electricity the following transformations would be realized: quinone (solid) $+ H_2 \longrightarrow$ hydroquinone (solid). The potential of this combination thus enables us to calculate directly the free energy of reduction referred to the 2 solid states. This free energy change and the corresponding reduction potential are independent of the solvent employed. In the case of tetrachloro-benzoquinone such a cell can actually be constructed and the potential determined. If the quinone, however, forms a quinhydrone with the corresponding hydroquinone, a saturated solution of the two substances cannot usually be formed without the separation of solid quinhydrone. In this case it is experimentally necessary to measure two separate combinations: one, a half-cell containing a solution saturated with the quinone and quinhydrone, and another containing a saturated solution of the hydroquinone and quinhydrone. One-half the sum of these two potentials $(\pi_q$ and $\pi_h)$ is the reduction potential referred to the change from solid quinone to solid hydroquinone (π_s) .

2 Quinone (solid) +
$$H_2 \longrightarrow$$
 Quinhydrone (solid) + 2 $F_{\pi q}$ (1)

Quinhydrone (solid) +
$$H_2 \longrightarrow 2$$
 Hydroquinone (solid) + $2 F\pi_h$ (2)

Adding (1) and (2),

Quinone (solid) + H₂
$$\longrightarrow$$
 Hydroquinone (solid) + $\frac{2F(\pi_q + \pi_h)}{2} = 2 F\pi_s$
or $\pi_s = \frac{\pi_q + \pi_h}{2}$ (3)

In two cases in which the quinhydrone formed only slowly in aqueous solution it was possible to measure π_s directly and also to calculate it from the quinhydrone cells; the agreement was very satisfactory.

² Conant and Fieser, This Journal, 44, 2480 (1922).

A subtraction of (2) from (1), on the other hand, gives,
2 Quinone (solid) + 2 Hydroquinone (solid)
$$\longrightarrow$$

2 Quinhydrone (solid) + 2F ($\pi_q - \pi_h$) (4)

Thus, the difference between the potentials of the two combinations is a measure of the free energy of the formation of the solid quinhydrone from its solid components.

Such measurements are novel, in the case of benzoquinone itself, only in their application to the determination of the free energy of the reduction referred to the solid state. Granger and Nelson³ saturated acid with hydroquinone and quinone in order to establish a definite ratio of quinone to hydroquinone in their verification of the logarithmic shape of the reduction curve. Sörensen¹ showed that solutions of sodium chloride saturated with quinhydrone and quinone, or quinhydrone and hydroquinone, gave constant potentials independent of the amount of salt present; these potentials were in close agreement with the values calculated from the solubility data which he experimentally determined. Biilmann and Lund4 gave further evidence of this constancy and proposed the terms "quino-quinhydrone" and "hydro-quinhydrone" to describe the two electrodes that were free from the "salt error." They calculated the free energy of formation of quinhydrone at 18° but did not calculate the free energy of formation of solid hydroquinone from solid quinone.

Experimental Procedure

The normal potential in solution (π_0) was measured for all the quinones in alcoholic solution, and in aqueous solution when the solubility was sufficient, by electrometric titration with titanous chloride. This method has been thoroughly investigated⁵ and has been recently applied to the determination of reduction potentials in mixtures of alcohol and aqueous acid.² The normal potential was found by interpolation of the titration curve to 50% reduction. As an indication of the slopes of these curves the difference between this potential and that at 20% and 80% reduction is given, in millivolts, under the headings $\Delta \pi_1$ and $\Delta \pi_2$. The theoretical value is 18 mv. All of these measurements were made at 25°.

We have previously shown that the normal potential is the same whether 50% or 95% alcohol is the solvent. Consequently, the one or the other concentration was used, according to the solubility of the quinone in question, the lower one being employed when possible in order to obtain better conductivity. Since π_0 often varies with the concentration of hydrochloric

² Granger and Nelson, This Journal, 43, 1401 (1921).

⁴ Biilmann and Lund, Ann. chim., 16, 321 (1921).

⁵ (a) Mansfield Clark, J. Washington Acad. Sci., 10, 255 (1920). (b) Conant, Kahn, Fieser and Kurtz, This Journal, 44, 1382 (1922). (c) LaMer and Baker, ibid., 44, 1954 (1922).

acid, it was desirable to investigate this variation at least to the extent of using 2 different acid concentrations for the measurements. In aqueous solution the acid was 0.1~N and 1.0~N, but the presence of a large amount of alcohol so decreases the conductivity that the more dilute solution was replaced by 0.5~N hydrochloric acid. This variation in π_0 with relatively small changes in acid concentration gives an indication of the susceptibility to such changes of the quinone-hydroquinone solubility ratio.

A weighing bottle of 25cc. capacity, fitted with a bright and a platinized platinum electrode, formed a convenient half-cell for carrying out the measurements which involved the use of saturated solutions. It was connected by a siphon plugged with filter paper to a Hildebrand hydrogen electrode vessel containing the same solvent as that used for making the saturated solution. The solids to be investigated were mixed with the solvent in this bottle which was then rotated in a thermostat at 25°. Potential measurements were made after the mixture had been shaken for different lengths of time; the constancy of repeated measurements was an indication that the solution was saturated with respect to both components.

Another method of insuring saturation was first to prepare a solution at $40-50^{\circ}$ and after cooling it to the temperature of the bath, measure the potential. The latter was the more convenient method and always gave consistent results. All solutions measured at 0° were first saturated at 25° .

The choice of the solvent to be used in these cells containing solid substances depended on many factors. Aqueous solutions were employed when possible owing to the greater conductivity thus obtained. Even $0.1\ N$ hydrochloric acid adds to quinone slowly, and the reaction might occur with a velocity sufficient to vitiate the results if stronger acid were employed.

In solutions less concentrated than $0.1\ N$ the hydrogen-ion concentration is perceptibly changed when the acid is saturated with hydroquinone. Therefore, $0.1\ N$ hydrochloric acid was used when possible. In the case of compounds that were too insoluble in water, aqueous alcoholic solutions were employed. It was found necessary to do this only with the tetra-substituted quinones; these substances do not add hydrogen chloride and, consequently, stronger hydrochloric acid could be used to insure better conductivity with no injurious effects.

In most cases, the potential was constant a few minutes after the cell was connected; a bright platinum, a gold plated and a platinized electrode gave identical readings. Several measurements were made with each cell after the potential had become constant. Each potential reported in the experimental portion of this paper represents the average value for each cell independently prepared. The reduction potential referred to the solid state (π_s) was calculated from the average of all the cells measured in the manner explained above.

The potential for each cell is reported to 0.1 mv. when the constancy of the electrodes permitted such a degree of accuracy. The final averages

⁶ Granger, Dissertation, Columbia University, March, 1920.

are reported to the nearest millivolt, as for most of the compounds the results are not significant beyond this figure and the potentiometer employed could not be relied on to more than 0.5 mv. The value of the hydrogen electrode was not corrected for dry hydrogen under standard conditions, as this correction is beyond the limit of accuracy of the present work. The accuracy of the measurements varies greatly with the substances investigated as can be seen by examining the concordance of the different determinations. The exact details of the experiments depended to such a great extent on the nature of the quinone in question that the results for each compound will be given separately.

Experimental Results

Benzoquinone.—The quinone and hydroquinone employed melted at $112-113^{\circ}$ and 169° , respectively. Quinhydrone was prepared according to the method of Biilmann and Lund⁴ by the partial oxidation of hydroquinone. Quino- and hydro-quinhydrone half-cells were prepared by saturating the 0.1~N acid with both components simultaneously.

BENZOQUINONE 0.1 N HCl Saturated with quinhydrone and Ouinone Hydroquinone Quinone Hydroquinone -At 25°v. 0.74900.61290.76980.6270.6275.7483.6118 .7698.7490.6132.7700 .6126. 7488 .6126.7699.6272Av.

The potentials of the individual cells interpolated to 18° agree very well with the determinations of Sörensen and of Biilmann in the papers previously referred to. Thus the value of π_s at 18° is found to be 0.6867, while Sörensen's results give 0.6869, Biilmann's 0.6870. Granger and Nelson's measurements,³ calculated to a suitable basis, give an average value for the hydro-quinhydrone electrode at 25°, of 0.6123, as compared with our number of 0.6126.

 $\pi_s = 0.699$

Toluquinone.—The quinone was prepared by steam distillation of a mixture of o-toluidine, manganese dioxide and sulfuric acid (1:4); it was recrystallized from alcohol; m. p., 67–68°; yield 15%. Eastman's toluhydroquinone, (m. p., 124–125°) was employed. The quinhydrone was prepared either by shaking the components with water or by mixing their alcoholic solutions, adding a little water, and allowing the green crystals to form. When washed with water and dried it melted at 99–100° with decomposition. Siegmund reports the melting point as 96–97°,

 $\pi_s = 0.681$

⁷ Clark, Am. Chem. J., 14, 565 (1892).

⁸ Siegmund, J. prakt. Chem., [2] 92, 359 (1915).

while Nietzki⁹ gives 52°. There are many such discrepancies in the literature, so that it appears likely that these melting points or points of decomposition are not characteristic of purity of quinhydrones.

TOLUQUINONE 0.1 N HCl Saturated with quinhydrone and Hydroguinone Quinone Hydroguinone v. 0.6620 0.5840 0.6770 0.6094 .6598 .5835 .6095 .6768 .6617 .5857 .6776 .6098 Av. .6612.5844.6771 .6096 $\pi_s = 0.623$ $\pi_s = 0.643$

p-Xyloquinone.—Siegmund⁸ states that p-xyloquinhydrone was not formed on applying the general method used in the preparation of other alkyl quinhydrones. Consequently, an electrode saturated with both quinone and hydroquinone was employed, and no evidence of the formation of a quinhydrone was observed in the potential measurements.

The p-xyloquinone used was Kahlbaum material and melted at 123.5°. For the preparation of the hydroquinone it was moistened with alcohol and a solution of stannous chloride containing hydrochloric acid was added. After the mixture had been thoroughly stirred, it was warmed on the steam-bath to complete the reduction. This caused the separation of a hard, black substance which, however, soon changed to the white hydroquinone and dissolved. The solution was boiled with animal charcoal and filtered, when p-xylohydroquinone separated in long, white needles; yield, 65%. It was completely pure, melting at 111.5°. This method of reduction is very convenient and is of general applicability.

Half-cells were prepared both by saturating the acid with a mixture of the solids and by mixing their saturated solutions and reading the potential immediately. Both methods gave the same result. In some cases the bright platinum and platinized electrodes were as much as 1 or 2 mv. apart, probably because of the slight solubility of the compounds. In these cases average values are reported.

p-XYLOQUINONE 0.1 N HCl Saturated with the quinone and the hydroquinone Volts at 25° 0.5826 0.5820 0.5821 0.5801; π_s = 0.582 Volts at 0° 0.5988 0.6003 0.6000; π_s = 0.600

MEASURE	ments in A	LCOHOLIC SC	LUTION BY	THE TITRATIO	ON METHOD	
HCl N	Alcohol	$\Delta \pi_1$ Mv.	$\Delta\pi_2$ Mv.	$\overset{\Delta\pi_0}{ ext{V.}}$	Av. V.	
0.5	95	17	23	0.598	0.600	
0.5	50	18	22	.601 {	0.000	
1.0	50	17	21	.597	.597	
1.0	50	19	21	.596 ∫		

⁹ Nietzki, Ber., 10, 834 (1877).

Duroquinone (Tetramethylbenzoquinone).—The authors are greatly indebted to Dr. Lee I. Smith, of the University of Minnesota, for the sample of duroquinone (m. p., 110–111°) used in this work. It was reduced with stannous chloride in the manner previously described, except that a large volume of water (2 to 3 liters per g.) was required to dissolve the hydroquinone. Durohydroquinone crystallized from water in pure white, lustrous plates melting at 226–227°. This compound, prepared by reducing the quinone with zinc and sodium hydroxide, sodium amalgam and alcohol, zinc and glacial acetic acid, and aniline, is reported as melting at 210°, 10° 220°11° and 210–224°, 12° and is said to be reoxidized by the air. No such oxidation was observed. The low reduction potential of the quinone (comparable with that of phenanthraquinone) would lead one to expect that the hydroquinone would be oxidized by the air but, since the reduction of the quinone is probably slow, the reverse process is probably also slow, presumably because of steric hindrance of the methyl groups.

The potential of this compound, which forms no quinhydrone, could not be measured in aqueous solution, apparently because of the very slight solubilities of the components. Consequently, measurements were carried out in aqueous alcohol containing 1.0 mole of hydrogen chloride per liter. The electrodes came rapidly to a definite equilibrium.

Duroquinone 50% Alcohol saturated with the quinone and the hydroquinone Volts at 25° 0.4800 0.4796 0.4801; π_s = 0.480 Volts at 0° 0.4990 0.4988 0.4996; π_s = 0.499

Duroquinone is too insoluble to permit titrations in aqueous solution. Titrations in alcohol were rendered somewhat tedious by the tardiness with which equilibrium was established. After each increment of reducing agent was added the potential fell 100 or 200 mv. (towards the titanous-titanic potential level) and then rose slowly to a constant value. It should be noted that the results of this slow titration are entirely consistent with the potential of a saturated solution of the quinone and hydroquinone; there can be no doubt that the titration is valid even with such refractory substances as duroquinone.

MEASUR	REMI	ents in Alcoi	HOLIC SOLUTION I	BY THE TITEA	TION METHOD
HC1 N		$\Delta \pi_1$ Mv.	$\Delta\pi_2$ Mv.	$\overset{\pi_0}{\mathrm{V}}$.	Av. V.
0.5		15	25	0.468	
0.5		15	19	.466	0 466
1.0		16	14	.467	0.466
1.0		17	19	.464	

¹⁰ Nef, Ann., 237, 6 (1887).

¹¹ v. Pechmann, Ber., 21, 1421 (1888).

¹² Rügheimer and Hankel, ibid., 29, 2174 (1896).

Thymoquinone.—Kahlbaum's thymoquinone, m. p., 45.5°, was reduced with stannous chloride in the usual way, giving long, white needles; m. p., 141.5°; yield, 88%. The usual procedure, using sulfur dioxide, 13 takes from 3 to 4 days and yields a dirty white product which, when purified, melts at 139.5°. Thymoquinhydrone was prepared by allowing a mixture of the ethereal solutions of equivalent weights of the components to evaporate very slowly. The lustrous, dark green crystals melted at 78° with decomposition.8

Electrode equilibrium was at times erratic in both cells, and both the bright and platinized types of electrodes often gave inconsistent, inconstant values. On the other hand, both types often became perfectly constant at the same point, so that there was no doubt when true equilibrium had been reached.

THYMOQUINONE

	0.1 2	V HCl Saturated wit	h the quinhydre	one and
	Quinone	Hydroquinone	Quinone	Hydroquinone
	A	t 25°	A	t 0°
	v.	v.	v.	v.
	0.5928	0.5660	0.6055	0.5922
	.5930	.5649	.6045	.5910
	. 5927	.5661	.6050	.5920
Av.	.5928	. 5657	.6050	. 5917
	$\pi_s = 0.5$	579		$\pi_s = 0.598$

Measurements in 50% Alcoholic Solution by the Titration Method

HC1 N	$\Delta \pi_1$ Mv.	$\Delta \pi_2$ Mv.	$\overset{\pi_0}{\mathrm{V}}$.	Av. V.
0.5	16	19	0.591	
0.5	17	19	.589	0 500
1.0	18	18	.589	0.589
1.0	16	19	.587	

Monochloroquinone.—Monochlorohydroquinone was prepared¹⁴ in a 74% yield by passing dry hydrogen chloride into a chloroformic solution of benzoquinone. When recrystallized from chloroform it melted at 101–102°. Oxidation by Clark's method proved convenient for small quantities and gave a 56% yield. By oxidation with potassium dichromate and extraction with benzene as in the method that has been developed for quinone, ¹⁵ an 84% yield was obtained, but the method was not as rapid. The compound was recrystallized from alcohol and melted at 57°. The quinhydrone was best prepared by the partial oxidation of the hydroquinone with ferric ammonium sulfate in aqueous solution. The bronzegreen needles melted at 67° ¹⁶ with decomposition.

¹⁸ Carstanjen, J. prakt. Chem., [2] 3, 54 (1871).

¹⁴ Levy and Schultz, Ann., 210, 138 (1881).

¹⁵ "Organic Syntheses," John Wiley and Sons, 1922, Vol. II, p. 85.

¹⁶ Ling and Baker [J. Chem. Soc., 63, 1314 (1893)] obtained a hydrate melting at $70-72^{\circ}$.

Difficulty was experienced in the measurement of the potentials of both this compound and 2,3-dichloroquinone because of the unusually great solubility of their hydroquinones. In $0.1\ N$ hydrochloric acid at 25° the solubility of hydroquinone is $0.0696\ g$. per cc.³ while that of monochlorohydroquinone is about $0.7\ g$. per cc. Even at 0° both the monochloro- and 2,3-dichlorohydroquinones are so soluble that they form deep red, sirupy solutions in which potential measurements would be very unreliable. This difficulty was to a large extent obviated by using $0.1\ N$ hydrochloric acid saturated with sodium chloride as the solvent, thus depressing the solubilities of the organic compounds to a very considerable extent. In this way results were obtained which, though perfectly reliable, are not of the highest degree of accuracy since the bright and platinized electrodes gave measurements sometimes as much as $2\ mv$. apart. Averages are reported in the following tables.

Monochloroquinone

	0.1 N	HCl Saturated with I	NaCl, the quint	ydrone and
	Quinone	Hydroquinone	Quinone	Hydroquinone
	A	t 25°	A	t 0°
	v.	v,	v.	v.
	0.722	0.635	0.740	0.651
	.721	.634	.740	.652
	.723	.634	.741	.651
Av.	.722	.634	.740	.651
	$\pi_s = 0.6$	78	π	$_{s} = 0.696$

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MEASUREMENTS	IN	ALCOHOLIC	COLUTION	В¥	THE	LITRATION	METHOD

HC1 N	Alcohol	$\Delta \pi_1$ Mv.	$\Delta \pi_2$ Mv.	$\overset{\boldsymbol{\pi o}}{\mathbf{V}}.$	Av. V.
0.2	50	17	20	0.736	
0.2	50	17	20	.736 (0.736
1.0	50	18	16	.735 ∫	0.750
1.0	95	18	16	.737 }	

2,6-Dichloroquinone.—This compound, prepared ¹⁷ by oxidizing trichlorophenol with chromic acid (69% yield), was crystallized from alcohol and from glacial acetic acid. Both samples melted at 120.5° . It was reduced, with 80% yield, to the hydroquinone which was crystallized from benzene and melted at 161° .

All of the dichloroquinones form quinhydrones, but not as readily as does benzoquinone. The 2,5 and 2,6 derivatives, described by Ling and Baker, 16 are of such an ill-defined character that they are scarcely suited to potential measurements. The 2,5 derivative forms a violet hydrate which, on drying, changes into a pale yellow, anhydrous quinhydrone. The quinhydrone of the 2,6 isomer is variously described as brown powder, dark needles, and brown prisms with a reddish shimmer.

An anhydrous quinhydrone cannot be used in our half-cell if not in ¹⁷ Kehrmann, J. prakt. Chem., [2] 40, 481 (1889).

equilibrium with the solvent used. The best way to insure that such equilibrium is maintained is to prepare the quinhydrone in the solvent concerned, add an excess of the quinone or hydroquinone, and measure the potential when the solution is completely saturated. This method was used with 2,6-dichloroquinone, and the results are indicated below.

2,6-Dichloroquinone

	0.1 1	V HCl Saturated with	the quinhydrone	e and
	Quinone	Hydroquinone	Quinone	Hydroquinone
		t 25°	At	0°
	v.	v.	V.	v.
	0.730	0.667	0.744	0.687
	.720	.669	.735	. 692
	.726	.670	.744	.691
	.727	• • •	.747	
Av.	.726	. 669	.743	.690
	$\pi_s = 0.6$	98	π_{i}	=0.717

These results are decidedly irregular but π_s , being an average value, is probably correct within a few millivolts, and it is certainly accurate enough for purposes of comparison. That the results obtained in saturated solution for all of the dichloroquinones are thus less accurate than those for the other compounds studied seems to be due wholly to the character of the quinhydrones which they form. It soon appeared that even the method employed above could not be used for the other isomers, since the quino- and hydro-quinhydrone electrodes gave quite varying potentials, indicating that the quinhydrone or its hydrate was not of constant composition. But since these quinhydrones do not form as readily as does the 2,6-derivative, it was found possible to mix saturated solutions of the quinone and hydroquinone and obtain reproducible readings before any quinhydrone separated. This method was proved valid in the measurements of trichloroguinone, when both this procedure and the one using the quinhydrone gave the same value for π_s . For further confirmation and for purposes of verifying the above results obtained with

2,6-DICHLOROQUINONE

MEASUREMENTS	IN 95% AL	COHOLIC SOL	UTION BY THE T	ITRATION METHO
HC1 N	$\Delta \pi_1$ Mv.	$\Delta \pi_2$ Mv.	$\overset{\boldsymbol{\pi_0}}{\mathrm{V}}.$	Av. V.
0.5	14	23	0.746	
0.5	14	20	.748	0.748
1.0	12	22	.752	
1.0	15	22	.748	
Measurem	ents in Aqu	eous Solut	ION BY THE TIT	RATION METHOD
0.1	17	19	0.722	0.722
0.1	17	18	.723 ∫	0.122
1.0	18	19	.719 \	0.719
1.0	18	17	.719 ∫	U.119

2,6-dichloroquinone, measurements were made on half-cells prepared by mixing saturated solutions of the two components. The values found for π_s were, at 25°, 0.697, 0.699, 0.692 (compare 0.698), and at 0°, 0.715, 0.714 (0.717). Because of the rapidity of precipitation of quinhydrone, the first values reported are considered to be more nearly correct.

These results are in good agreement with determinations made by Baker¹⁸ which gave the value 0.7210 for 0.2~N hydrochloric acid. Her sample was prepared from 2,6-dichloro-p-aminophenol.

2,3-Dichloroquinone.—2,3-Dichloro-hydroquinone was obtained by Peratoner and Genco by the action of sulfuryl chloride on hydroquinone ^{19a} and by the reduction of quinone dichloride with sulfur dioxide. ^{19b} They also observed that this compound was a by-product in the preparation of 2,5-dichloro-hydroquinone from monochloroquinone and hydrochloric acid. Oliveri-Tortorici²⁰ obtained a 12% yield by the last-named method and pointed out that the other two processes are not only troublesome but give rise to a variety of by-products. Den Hollander²¹ recently repeated the experiments of the Italians but was unable to obtain any of the desired compound. On saturating a cooled ethereal solution of monochloroquinone with dry hydrogen chloride he obtained a mixture that he could not separate by fractional crystallization from benzene but which he identified by oxidation and separation of the quinones as a mixture of the 2,5 and the 2,6 isomers.

Under apparently identical conditions we obtained, after fractional crystallization from benzene, 2,3-dichloro-hydroquinone (melting at 137°) and monochlorohydroquinone. The products of the reaction are thus difficult to control.

A satisfactory method, however, has recently developed in the work of Eckert and Endler²² on the chlorination of hydroquinone in glacial acetic acid. Since their interest lay in finding a suitable method for the preparation of the 2,5-isomer, their directions were examined and modified as follows.

Forty g. of hydroquinone was suspended in 200 cc. of glacial acetic acid and treated with chlorine at $40-50^{\circ}$ until the solution had gained 33 g. of chlorine (30% excess). Only a small amount of crystals formed on cooling and the liquid was concentrated in a vacuum. The crystalline paste was dissolved in water and filtered hot to remove a small amount of insoluble tetrachloro-hydroquinone. The filtrate was boiled with animal charcoal and filtered hot. As the solution cooled, 28 g. of rose-colored

¹⁸ Baker, Dissertation, Columbia University, August, 1922.

^{19 (}a) Peratoner and Genco, Gazz. chim. ital., [2] 24, 376 (1894); (b) p. 388.

²⁰ Oliveri-Tortorici, ibid., [2] 27, 584 (1897).

²¹ Den Hollander, Rec. trav. chim., 39, 481 (1920).

²² Eckert and Endler, J. prakt. Chem., [2] 104, 81 (1922).

crystals separated which lost water at 100° and melted at 138–139°. When these were dried in benzene and crystallized, 19.5 g. of white crystals was obtained that melted at 143°; 9 g. was recovered from the various filtrates but was not purified; total yield, 43%; yield of pure product, 30%.

Oxidation to the quinone was accomplished by Clark's method with an 88% yield. The product crystallized from alcohol in long needles melting at 100-101° (the melting point given is 96-98°).

Measurements with this compound were made in 0.1 N hydrochloric acid saturated with sodium chloride as in the case of monochloroquinone, because of the extreme solubility of the hydroquinone. Cells containing the red quinhydrone (probably a hydrate), which is formed on shaking the components with the solvent, were variable and inconstant, but a mixture of the saturated solutions of the components was sufficiently stable to permit measurements to be made. The length of time during which the potential remains constant (before the quinhydrone starts to separate) is, of course, dependent on the many factors that initiate the crystallization of a supersaturated solution. Inoculation by minute crystals adhering to the apparatus used in a previous experiment invariably caused the potential to drop and the red quinhydrone hydrate to separate in 1 to 2 minutes. But even when all precautions in regard to cleaning the apparatus were taken, crystallization often began before a large number of readings could be made, especially at 0°, and especially when the halfcell had to be shaken to obtain true equilibrium at the platinum surfaces.

2,3-DICHLOROQUINONE 0.1 N HCl Saturated with NaCl, the quinone and the hydroquinone Volts at 25° 0.675 0.676 0.675; π_s = 0.675 Volts at 0° 0.691 0.693 0.692; π_s = 0.692

]	Measur	EMENTS	1095%	ALCOHOLIC SOLUTI	ON BY THE	TITRATION METHO
	HCI N		$\Delta \pi_1$ Mv.	$\Delta\pi_2$ Mv.	$_{ m V}^{\pi o}$	Av. V.
	0.5		16	18	0.740	0.739
	0.5		14	15	.738	(0.109
	1.0		- 8	16	.711	711
	1.0		10	16	.710	

ME	SASUREMENTS	IN AQUE	ous Solution	BY THE	TITRATION	Метног
	0.1	17	19	.708)	708
	0.1	17	17	.708		.708
	1.0	17	21	.703	ſ	704
	1.0	18	17	.705		.70±

2,5-Dichloroquinone.—The crude hydroquinone (m. p., $156-159^{\circ}$) was obtained from hydroquinone and potassium chlorate in 68% yield by the directions of Ling.²³ Monochlorohydroquinone (m. p., $100-105^{\circ}$) was

²³ Ling, J. Chem. Soc., 61, 558 (1892).

obtained from the filtrate as a by-product. The dichloro-hydroquinone was recrystallized from benzene and melted at 166°.

It was oxidized in the cold with dichromate and sulfuric acid, and the quinone, recrystallized from alcohol and washed with ether, melted at 158.5°. It is necessary to wash with ether and dry rapidly, for otherwise the surfaces of the crystals become darkened with the formation of the quinhydrone.

Potential measurements were carried out on mixtures of the saturated solutions of the quinone and hydroquinone. Quinhydrone formation was so slow that concordant results were also obtained by stirring the acid with the two solids at 25°.

2,5-DICHLOROQUINONE 0.1 N HCl Saturated with the quinone and the hydroquinone Volts at 25° 0.686 0.692 0.693 0.689 0.688 0.689; $\pi_s = 0.689$ Volts at 0° 0.708 0.711 0.711 0.709 0.709; $\pi_s = 0.710$

MEASUREMENTS	IN	95%	Alcoholic Solution	$_{\rm BY}$	THE	TITRATION	Metho	Œ
HCl		$\Delta \pi_1$	Δπ2	πο		A	v.	
N		Mv.	Mv.	V.		V	r .	

N	Mv.	Mv.	v.	v.
0.5	10	20	0.740 \	0.740
0.5	10	17	.740 ∫	0.740
1.0	11	23	.735 \	794
1.0	10	20	.733 ∫	.734

MEASUREMENTS	IN AQUEOUS	Solution by	THE TITRATION	Метнор
0.1	19	21	.719	
0.1	18	18	.722 (.719
1.0	18	20	.718 ∫	.719
1.0	17	19	.718	

Trichloroquinone.—Kahlbaum's trichloroquinone (m. p., 162–163°) was reduced with stannous chloride and the hydroquinone crystallized from glacial acetic acid. After removal of the acetic acid of crystallization in a vacuum desiccator the compound melted at 136°. By the spontaneous evaporation of a chloroformic solution of the components, trichloroquinhydrone was obtained in well-formed clusters of green-black crystals melting²⁴ at 114–115°.

Half-cells were prepared by stirring a suspension of the quinone and hydroquinone in $0.1\ N$ hydrochloric acid at 25° for as long as 15 hours and by cooling from a higher temperature; no quinhydrone formation was observed. On cooling to 0° , however, small amounts of this compound separated, so that when working at this temperature the solids were dissolved separately and the solutions mixed. Such a half-cell was stable for 1 to 2 hours. Though the quinhydrone is formed with difficulty in

²⁴ Ling and Baker (Ref. 16) obtained by this method a compound melting at 103°. Of their other preparations, the highest-melting compound (115-117°) analyzed for ¹/₂ H₂O but did not lose water over coned. sulfuric acid.

the presence of water, electrodes containing previously prepared quinhydrone were stable at 25°. The potentials of a quino- and a hydroquinhydrone half-cell were 0.6811 and 0.6612, from which $\pi_s = 0.671$, in good agreement with the following results.

TRICHLOROQUINONE

0.1 N HCl Saturated with the quinone and the hydroquinone
 Volts at 25° 0.6695 0.6698 0.6696; π_s = 0.670
 Volts at 0° 0.6904 0.6905 0.6902; π_s = 0.690

Measurements in 95% Alcoholic Solution by the Titration Method

N	$\Delta\pi_1 \ \mathbf{Mv}$.	$\Delta\pi_2$ Mv.	$\overset{\boldsymbol{\pi_0}}{\mathrm{V}}.$	Av. V.
0.5	12	18	0.733 \	0 701
0.5	13	20	.730 ∫	0.731
1.0	11	16	.724 $)$.726
1.0	11	14	.728 ∫	.120

Tetrachloro-benzoquinone.—Tetrachloroquinone (m. p., 283-284°) was reduced with stannous chloride in the usual way. The hydroquinone was repeatedly crystallized from glacial acetic acid, dissolved in this solvent, and precipitated with alcohol. It melted constantly at 230-231°.

Half-cells saturated with the quinone and the hydroquinone were employed. Though both components are almost insoluble in water, measurements in $0.1\ N$ acid could be carried out, although equilibrium was established with some difficulty, especially at 0° .

Thus, at 0° one cell, on long standing, reached a potential about 4 mv. above the recorded value, while the other cell under similar conditions was 4 mv. below this value. When the cell was shaken, the potential of each came to about the same (the recorded) value. Slight polarization apparently causes appreciable concentration changes in these dilute solu-

TETRACHLORO-BENZOQUINONE

SATURATED SOLUTIO	ONS OF THE QUINONE AND	THE HYDROQUINONE
25° V.		0° V.
$0.6641 \ 0.6638 \ $	0.1 N HCl	∫ 0.6830 0.6838
0.6640 \	50% alcohol,	∫ 0.6830
0.6622	1.0 N HCl	0.6825
$\pi_s = 0.664$		$\pi_{\rm s} = 0.683$

Measurements in 95% Alcoholic Solution by the Titration Method

HC1 N	$\Delta \pi_1$ Mv.	$\Delta \pi_2$ Mv.	$\overset{\boldsymbol{\pi_0}}{\mathrm{V}}.$	Av. V.
0.5	11	16	0.694	
0.5	14	24	.696	0.695
0.5	14	25	.695	
1.0	15	25	.704	
1.0	15	21	.703	.703
1.0	13	27	.703	

tions. It was more convenient to use aqueous alcohol as the solvent, although even in this case, electrode equilibrium was not of the best and both types of electrode were occasionally erratic. The agreement of the results in aqueous and in aqueous-alcoholic solution constitutes a good proof of the constancy of this quinone-hydroquinone electrode.

The Potentials Referred to the Solid and Dissolved States

A summary of the results obtained is given in Table I. A few values, the details of which do not appear above, are taken from a previous paper.² The potentials of benzoquinone, toluquinone, monochloroquinone and 2,6-dichloroquinone in dil. acid have also been determined by other investigators and our results agree with theirs within 1 mv. except in the case of toluquinone; for this compound the more accurate value of Biilmann²⁵ is given preference to our number of 0.6435. The two starred figures are taken from the results of LaMer and Baker^{5c} who used 0.2 N hydrochloric acid as solvent. In the two columns under the normal potential for each of the solvents two values are given when π_0 varied with the acid concentration beyond the limits of experimental error. When but one figure is given under the heading "1.0 N HCl," it indicates that such variation was not observed.

Table I Reduction Potentials at 25°

	Solid state		In solution			
	$egin{array}{c} \pi_s \ \mathrm{V}. \end{array}$	$\Delta \pi_s 0^{\circ} - 25^{\circ}$ My.	πο (wa 0.1 N HCl V.	iter) 1.0 N HCI V.	$0.5 \frac{\pi_0}{N}$ (all HCl V.	eohol) 1.0 N HCl V.
Benzoquinone	0.681	-18	0.699	0.696		0.711
Toluquinone	.623	-20	.645	.641		.656
p-Xyloquinone	.582	-18	.590*		. 600	. 597
Duroquinone	. 480	19				.466
Thymoquinone	. 579	19	.588*			.589
Monochloroquinone	. 678	-18	.713	.710	,	.736
2,3-Dichloroquinone	.675	-17	.708	.704	.739	.711
2,5-Dichloroquinone	.689	-21		.719	.740	.734
2,6-Dichloroquinone	.698	 19	.722	719		.748
Trichloroquinone	.670	-20			.731	.726
Tetrachloroquinone	.664	-1 9			.695	. 703

It will be observed from the table that the potentials for the three conditions exhibit a certain parallelism. This is shown more clearly in Fig. 1 in which the potentials are plotted against the number of substituents. For the dichloroquinone the *para* isomer was arbitrarily selected for plotting since its potential is always intermediate between those of the other two. In those cases in which π_0 varied with the acid concentration an average value was used for the purpose of characterizing each compound as completely as possible.

²⁵ Biilmann, Ann. chim., 15, 109 (1921).

The three lines for both the chlorine and methyl series are roughly parallel. In every case but one, the order of the potentials is: alcoholic solution > aqueous solution > solid state. With the tetramethyl com-

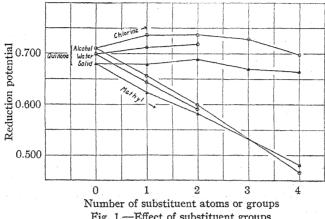


Fig. 1.—Effect of substituent groups

pound this order is reversed for the alcoholic solution and the solid state (the substance was not soluble in aqueous solution). It is evident from Fig. 1 that from the results obtained either in solution or referred to the

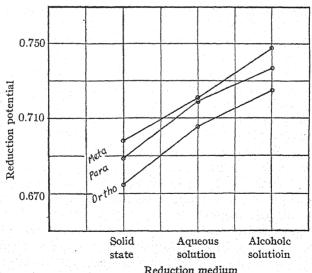


Fig. 2.—Dichloroquinones

solid state one would conclude: (a) that the introduction of methyl groups progressively and regularly decreases the potential, and (b) that the introduction of chlorine atoms first raises the potential and then lowers it even

below that of the parent substance. In Fig. 2, in which the potentials are plotted on an arbitrary scale, it is seen that even the subtle differences between the positional isomers are reflected in a nearly parallel manner by the potentials referred to the solid state, an aqueous solution or an alcoholic solution.

It will be further observed from Table I that all of the temperature coefficients of the potentials referred to the solid state have the same sign and are very nearly identical. It was shown in a previous paper² that this is also true of the temperature coefficients in aqueous and alcoholic solution. Therefore, relations based upon either π_3 or π_0 can reasonably be expected to hold at any temperature at which the comparisons may be made.

Thus, a definite answer has been obtained to the questions raised at the beginning of this article. The lines in Fig. 1 are so nearly parallel that one may safely say that the *relation between the potentials of a series of compounds* is very nearly the same whether the experiments are performed in aqueous solution, alcoholic solution or in saturated solutions.

We have been particularly anxious to settle this point in connection with our studies on the potentials of many naphthoquinone and anthraquinone derivatives which are too insoluble to be measured in aqueous solution either by the titration method or in saturated solutions. If the relationship in a series of quinones is essentially independent of the nature of the solvent we can safely proceed with our measurements of these insoluble substances in alcoholic solution. There is every reason to believe that the divergences from this simple generalization are greatest in the case of such benzoquinone derivatives as we have examine. The introduction of a substituent into the naphthoquinone or anthraq sinone nucleus would certainly change the ratio of the solubility of the quinone to the hydroquinone much less than the introduction of the same substituent into benzoquinone. In fact, evidence in regard to this point is already at hand; we have measured some 20 naphthoguinone and anthraguinone derivatives in alcoholic solutions containing 1.0 N and 0.5 N hydrochloric acid and the potential (π_0) was found to be the same in both solvents; this is in contrast to such benzoquinone derivatives as xyloquinone and the dichloroquinones. Another example of the relatively great susceptibility of the potential of benzoquinone derivatives to changes in the solvent is found by comparing the varying potential of benzoquinone in salt solutions1 with the consistency of the potentials of certain anthraquinone sulfonic acids in buffer solutions.5b

In considering those cases in which the relationship of the potentials of a series of compounds varies somewhat with the nature of the solvent, the problem arises as to which set of measurements is most significant. For example, in developing a general theory of the relation between con-

stitution and reduction potential, are the potentials of the chloroquinones in alcoholic solution (top line, Fig. 1) to be considered, or the potentials referred to the solid compounds (lowest line, Fig. 1)? In discussing the potentials of the isomeric dichloroquinones (Fig. 2), should one employ the results in alcoholic solutions or aqueous solution or those referred to the solid state? The potentials that are referred to the solid state (π_s) represent the algebraic sum of the free energy of three distinct processes, thus: $nF\pi_s = \Delta F$ (formation of dilute solution of quinone) + $nF\pi_0$ + ΔF (precipitation of the hydroquinone from dilute solution).

The introduction of a substituent into a quinone affects the value of all three terms on the right-hand side of this equation. We are concerned with the effects of substitution on the affinity of the quinone for hydrogen; since π_s includes not only this term but also the energy changes involved in passing from the two solid states into dilute solution, it is not an accurate measure of the relationship we are investigating. The ideal potential would be measured in a solvent in which both the quinone and the hydroquinone molecules are completely free from association or solvation of any sort; in other words, in a solvent in which the conditions of a perfect gas are realized. Under such conditions where the absolute activity26 was equal to the concentration, the potentials of a series of quinones would give a true measure of the effect of substitution on the affinity of the quinone for hydrogen. The values of π_0 obtained in aqueous or alcoholic solution are at present our best approximation to this ideal potential and probably give relationships which are only slightly in error. As the results in both solutions are almost parallel, one cannot go far wrong in deducing generalizations from either of them. For the present purpose it would be misleading to assign arbitrarily an activity coefficient of unity to the compounds in pure aqueous solution and refer our results to this standard; for all that we know at present, the absolute activity coefficient may be more nearly unity in alcoholic than in aqueous solution.

An examination of the experimental results obtained with the chloro-quinones shows the general consistency of the series of potentials in alcoholic solution (π_0) whereas the potentials referred to the solid state form an irregular series and they are related to the irregular solubility relationships of certain of the chlorohydroquinones. The potentials of the first 4-chloro compounds, both in alcohol and in water, are all higher than that of quinone itself; the relation is not additive, however, and the potential gradually falls with the presence of 3, then 4, chlorine atoms. In the experimental portion of this paper attention was called to the abnormal solubility of mono- and of 2,3-dichloro-hydroquinone. The potential of the latter compound in alcohol changes greatly with the acid concentration, an indication of a susceptible solubility ratio. But, al-

²⁶ Lewis, Proc. Am. Acad. Arts Sci., 43, 259 (1907).

though the ratios for these two compounds are anomalous, the relative positions of their potentials in solution fall in line with those of the other chloroquinones. This is not the case with π_s . Again the potential is low with 3 or 4 chlorine atoms present, and again the 2,5- and 2,6-dichloroquinones occupy a position above that of quinone. But mono- and 2,3-dichloroquinone, whose solubility ratios are abnormal, fall below the position of the parent compound. Thus, from the above data it appears that π_0 is more significant for the purposes of studying structure than π_s .

The main points of interest in connection with the problem of the relation between reduction potential and chemical constitution have already been pointed out in this discussion. It should be further noted that thymoquinone (Table I) has the same potential as p-xyloquinone and is very different from its structural isomer duroquinone. This disposes of the idea that the lowering of the reduction potential is a simple function of the molecular weight.27 The data at present available are not sufficient for any wide generalizations in regard to even benzoquinone derivatives; nevertheless the striking difference between the effects of methyl groups and chlorine atoms deserves special comment. Whereas the effect of the methyl group is progressively accumulative in lowering the potential, the introduction of chlorine atoms first raises then lowers the potential. The usual distinction between a "positive" methyl group and a "negative" chlorine atom harmonizes well with the decreasing potential of the methyl homologs and the increased potential of monochloroquinone. However, some other factor must be considered in explaining the potentials of the other chloroquinones. It will be very interesting to determine whether or not other "negative" groups or atoms behave in the same manner as the chlorine atom.

Comparison with Thermochemical Data

In 1900 Valeur²⁸ made an extensive study of the thermochemistry of quinones in which he measured the heats of combustion of the quinones and their hydroquinones and thus calculated the heats of reduction. Comparison of his values with the total energy of reduction in solution as found electrometrically has already been shown by Biilmann²⁵ and by the authors² to yield fairly concordant results in a few cases. From the above data $(\pi^{25^{\circ}}_{s})$ and $d\pi_{s}/dt$ it is now possible to compare Valeur's figures for the solid state (ΔH_{s}) with the same quantities calculated from potentials. Such a comparison is given in Table II. Two values are inclosed in brackets to indicate that they are of a lower degree of accuracy than the others, because of the difficulties referred to in the experimental portion of this paper.

²⁷ First advanced by Kehrmann, Ber., 31, 979 (1898).

²⁸ Valeur, Ann. chim., 21, 470 (1900).

Table II

Comparison of Thermochemical and Electrochemical Data

Total energy change of reduction

referred to the solid state (ΔH_s) Thermochem. (Valeur) Electrochemically Kj. Benzoquinone 175.1 172.8 Toluguinone 156.3 166.2 Thymoguinone 146.3155.4 Monochloroquinone (172.3)165.52,6-Dichloroquinone 140.9 (178.4)Trichloroquinone 93.2 175.3 Tetrachloroguinone 99.1 171.9

Since potential measurements are so likely to be free from large accidental or systematic errors, we are convinced that the great discrepancy which is evident from the table is due to both the great experimental difficulties in thermochemical work and the errors inherent in the calculations of the total energy change from the heats of combustion of the quinone and the hydroquinone. The heat of reduction is the small difference between the large heats of formation of quinone and of hydroquinone. Furthermore, an error in the heats of combustion of each substance is multiplied by the molecular weight and the two errors are additive. The accuracy of the thermochemical measurements is in most cases not very great. Thus for benzoquinone, which has been investigated by others29 besides Valeur, the mean of all the determinations shows a probable error of 8.7%. With other quinones, for each of which Valeur made 2 or 3 determinations, the error is always greater owing to the increased molecular weight. Valeur's two values for benzoquinone agree within less than 2%; and for the alkyl derivatives within 7%. Now, while these compounds were easily burned, great difficulties were experienced with the polychloro compounds; a correction for unoxidized chlorine had to be made and auxiliary combustible material evolving as much as 76% of the total heat had to be employed. Valeur's value for tetrachloroquinone is 42% lower than ours; while the difference is 47% for trichloroguinone, for which potential measurements show a high degree of accuracy. other chloro derivatives show similar, though smaller, deviations. thermochemical data must be considered to be greatly in error for these quinones.

Unfortunately, while Valeur was fully aware of the errors of his method and expressly stated that his results were but approximations, he made them the basis of conclusions as to the oxidizing power of quinones, which also involved the tacit assumptions of equal solubility ratios and of the truth of the Berthelot principle. Needless to say, these conclusions are

²⁹ Berthelot and Recoura, Ann. chim., [6] 13, 311 (1888). Berthelot and Longuinine, ibid., [6] 13, 333 (1888). Stohmann, J. prakt. Chem., [2] 45, 335 (1892).

at variance with the results of potential measurements and must be discarded.

Energy of Quinhydrone Formation

The total energy of formation of solid benzoquinhydrone from solid quinone and hydroquinone was calculated by Berthelot³⁰ from the heat of formation in solution and the heats of solution of the factors and the product. This same value may be calculated from the potentials and temperature coefficients of the quino- and hydro-quinhydrone electrodes. The potential (π_{qh}) corresponding to the free energy of the reaction, Quinone (solid) + Hydroquinone (solid) \longrightarrow Quinhydrone (solid), is calculated, as explained above, (Eq. 4) from the simpler relation, $\pi_{qh} = \pi_q - \pi_h$. From the data on p. 2198, the total energy change at 13° is found as follows.

$$\frac{\mathrm{d}\pi_{7h}}{\mathrm{d}t} = \frac{(0.749 - 0.613) - (0.770 - 0.627)}{25} = -0.00028 \text{ v.}$$

$$\Delta H = 96.5 \times 0.139 + 96.5 \times 286 \times 0.00028 = 21.1 \text{ kj.}$$

This is quite different from Berthelot's value of 37.1 kj. for the same temperature. In view of the general concordance of our electrochemical results with those of Sörensen and of Bilmann, it is not unlikely that the discrepancy is due to an error in the thermochemical measurements.

It has been pointed out ³¹ that the free energy of the reaction, Quinone (solid) + $H_2 \longrightarrow$ Hydroquinone (solid), is given by the expression,

$$\Delta F_s = 2F\pi_0 + RT \ln \frac{a}{b},\tag{5}$$

in which π_0 is the reduction potential referred to the dissolved state; a and b are the solubilities of quinone and hydroquinone, respectively, in a solution saturated with them both. This stipulation, that the solubilities employed be those of each compound in the presence of the other and not in solution by itself, was shown by Smits³² to be necessary in the application³³ of the van't Hoff equation for the shift in equilibrium constant with a change in solvent. Equation 5 simply states that to obtain the free energy of reduction in the solid state one must add to the free energy of reduction in solution $(2F\pi_0=RT\ln K)$ the free energy of bringing quinone from a saturated to a dilute solution $(RT\ln a)$ and of concentrating the dilute solution of hydroquinone $(-RT\ln b)$. The free energy of passing from the solid phase to a saturated solution is, of course, zero.

We may now expand this equation to include those cases in which simultaneous saturation of a solution with quinone and hydroquinone is not realizable. If k is the dissociation constant of quinhydrone and c its solubility, it is seen that, in any solution saturated with quinhydrone and

³⁰ Berthelot, Ann. chim., [6] 7, 203 (1886).

³¹ Ref. 2, p. 2490.

³² Smits, Z. physik. Chem., 92, 35 (1918).

³³ Dimroth, Ann., 377, 127 (1910).

(all solids). Thus:

one of its components, $k = \frac{a \times b}{c}$; $a = \frac{kc}{b}$; $b = \frac{kc}{a}$. These values for a and b may now be substituted in Equation 5 for a solution saturated with quinone in the first case and with hydroquinone in the second. An electrode dipping in the first solution records the potential corresponding to the free energy of reduction of quinone to quinhydrone (ΔF_q) ; in the second, the free energy of reduction of quinhydrone to hydroquinone (ΔF_p)

Quinone +
$$H \longrightarrow 1/2$$
 Quinhydrone: $\Delta F_q = \frac{1}{2} RT \ln K + \frac{1}{2} RT \ln \frac{a^2}{k_1 c}$ (6)

$$^{1}/_{2}$$
 Quinhydrone + $H \longrightarrow$ Hydroquinone: $\Delta F_{h} = \frac{1}{2} RT \ln K + \frac{1}{2} RT \ln \frac{k_{2}c}{h^{2}}$ (7)

Subtracting (quinone + hydroquinone → quinhydrone)

$$\Delta F_{qh} = \Delta F_q - \Delta F_h = RT \ln \frac{a \times b}{c} - \frac{1}{2} RT \ln k_1 k_2 \qquad (8)$$

In Equations 6 and 7 the dissociation constants used are the actual constants $(k_1 \text{ and } k_2)$ for quinhydrone when in the presence of a saturated solution of quinone and of hydroquinone, respectively. Granger and Nelson³ have shown that k_2 differs from k, the normal dissociation constant. Using their solubility data and their value for k_2 at 25° for 0.1 N hydrochloric acid and assuming at first that $k_1 = k$, ΔF_{qh} is found to have a value of 13.37 kj. This is higher than the value of 13.14 kj., found from the potential measurements and recorded in Table III. But, using the normal potential of quinone and the solubilities, in 0.1 N hydrochloric acid, with the same assumption concerning k_1 , ΔF_q and ΔF_h are found to be equal to 72.54 kj. and 59.16 kj. From our potential measurements these quantities are found to be 72.28 kj. and 59.16 kj., respectively. The lack of exact agreement in the values for ΔF_q indicates that the dissociation constant of quinhydrone is inconstant not only in the presence of an excess of hydroquinone but also in the presence of an excess of quinone.

Table III
Free Energy of Formation of Solid Quinhydrone from Solid Components

	259	•	0	٥ .	$\left(\Delta F_{qh}^{0} - \Delta F_{qh}^{25}\right)$	۰۱.
Quinhydrone of	V.	ΔF_{Qh} Kj.	$egin{array}{c} \pi_{qh} \ \mathrm{V}. \end{array}$	ΔF_{qh} Kj.	$\Delta F_{qh} - \Delta F_{qh}$ Kj.	qh)
Benzoquinone	0.136	13.1	0.143	13.8	-0.7	
Toluquinone	.077	7.4	.068	6.6	+0.8	1.
Thymoquinone	.027	2.6	.013	1.3	+1.3	
Monochloroquinone	.088	8.5	.089	8.6	-0.1	
2,6-Dichloroquinone	.057	5.5	.053	5.1	+0.4	
Trichloroquinone	.020	1.9				

Before examining Table III it should be pointed out that any conclusions based on the values given are rendered somewhat doubtful by the fact that the chloroquinhydrones undoubtedly exist in contact with aqueous solution in the form of hydrates. Consequently ΔF_{gh} represents the free

energy of formation and of hydration of the compounds in these cases. However, in relation to the above comparison of the affinity of reactions occurring in solution and in the solid state, it is perhaps significant that temperature coefficients indicated in the table vary so greatly as even to be of opposite sign. For benzoquinhydrone ΔF_{qh} decreases slightly with temperature while for thymoquinhydrone it is doubled in the same temperature interval and there is no indication of hydrate formation in either case.

Whether or not this is true of the free energy of formation of quinhydrones in solution cannot, at present, be decided. The latter quantity, calculated from the dissociation constants in water, is 3.3 kj. (25°) for benzoquinhydrone^{3,25} and 5.8 kj. for toluquinhydrone. The affinity of formation of the complex in solution is increased by the substitution of a methyl group while, when the total process involving the solids is considered, this group lowers the affinity. The first term in Eq. 8, $RT \ln \frac{a \times b}{c}$, is found by subtraction to be 10.1 kj. for benzoquinhydrone and 1.6 kj. for toluquinhydrone. The small value of this term indicates that the solubilities of its components. This rather surprising relationship is easily demonstrated by the fact that no toluquinhydrone precipitates when saturated solutions of its components are mixed. Benzoquinhydrone precipitates at once under these conditions, as the relatively large value of the "solubility term" indicates.

Since ΔF_{ab} , the free energy of formation of solid quinhydrone, is subject to wide variations in its temperature coefficient and because of the different solubility relations of a series of closely related compounds, it cannot be considered to be of much significance in the study of the structures of these complexes. It does give an indication of the "ease" with which the various quinhydrones are obtained. In order that a quinhydrone be obtained from a given solution of the components it is necessary that (1) they associate and that (2) the quinhydrone, being less soluble than its factors, precipitate. The total free energy, ΔF_{ab} , will be the same regardless of the solvent, so that if a solvent is chosen in which relatively great association takes place, the quinhydrone will not be so insoluble relative to its components in that solvent as in one in which association is less. Thus, one may prepare a quinhydrone by precipitation, by mixing the components in a solvent which favors precipitation, or by evaporation, if the solvent chosen favors association but not precipitation. Of course the quinhydrone may be made more insoluble by adding an excess of one of the components, according to the law of mass action, unless the quinhydrone is of the toluquinone type, when addition of a component precipitates the quinhydrone contaminated with that component.

It is interesting to notice that other investigators have observed the effect of these two factors, solubility and dissociation, in determining the course of the reaction, though the precise relationship was not seen. Torrey and Hunter³⁴ believed that the stability of the halogenated quinhydrones depends "on the number of halogens present only as this affects the solubility of the factors and of the quinhydrone itself." Jackson and Bolton,³⁵ finding that the quinhydrone of iodanil but not of chloranil could be prepared, and believing the solubility relations to be about identical in the two cases, held that the solubility relations play no part in the formation or non-formation of quinhydrones, but that the determining factor is the negativity of the substituent groups. Since this factor, the negativity, must determine dissociation, the two opposing views are now fused into one which maintains that both solubility and dissociation constants are important.

It will be observed that the figures in the table agree well with the known behavior of these quinhydrones. The free energy of formation of benzo-quinhydrone is the greatest of all and is decreased by the introduction of substituents, whether these are positive or negative. Tendency of formation vanishes with the introduction of 2 methyl groups or 4 chlorine atoms. It is well known that the stability of quinhydrones decreases with the number of halogen substituents, and that neither chloranil nor p-xyloquinone forms a quinhydrone with its hydroquinone.³⁶

We wish to acknowledge our indebtedness to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for two grants which have greatly assisted this work.

Summary

- 1. The question has been raised as to the relationship of the reduction potentials of a series of quinones in different solvents and referred to the solid state.
- 2. The reduction potentials of 4 alkyl derivatives and 6 chloro derivatives of benzoquinone have been measured in alcoholic solution, in aqueous solution (with three exceptions) and referred to the solid state.
- 3. Essentially the same relationships have been found whether the potentials measured in aqueous or alcoholic solutions were compared. The potentials referred to the solid state are not entirely parallel to those measured in solution. From these facts and general considerations it has been shown that in comparing the reduction potentials of a series of quinones the substances should ideally be measured in a solvent in which the absolute activity coefficient of the organic substances is unity; alcoholic

³⁴ Torrey and Hunter, This Journal, 34, 702 (1912).

³⁵ Jackson and Bolton, Ber., 45, 871 (1912); This Journal, 36, 304 (1914).

³⁶ Ref. 16. Schlenk, Ann., 368, 287 (1909).

or aqueous solutions seem to be sufficiently close to this ideal condition to make the measurements in these solvents significant.

- 4. The introduction of alkyl groups progressively lowers the reduction potential in the case of the 4 alkyl compounds investigated. The introduction of chlorine, on the other hand, first raises and then lowers the potential.
- 5. In order to measure the reduction potential referred to the solid state of those quinones that form quinhydrones, it was necessary to measure the potential of cells containing quinone-quinhydrone and hydroquinone-quinhydrone. The validity of this procedure has been demonstrated. Data concerning the energy of quinhydrone formation have been thus obtained.
- 6. The temperature coefficient of the reduction potential referred to the solid state has been measured for all of the quinones investigated and the total energy of reduction thus calculated. A comparison with previous thermochemical measurements shows great discrepancies in the case of the polychloroquinones; the cause for this discrepancy seems to lie in the errors inherent in the thermochemical measurements.

Cambridge 38, Massachusetts

NEW BOOKS

A Course of Laboratory Experiments on Physico-chemical Principles. By Miles S. Sherrill, Associate Professor of Theoretical Chemistry in the Massachusetts Institute of Technology. The Macmillan Co., New York, 1923. x+125 pp. Illustrated. 22.5×14.5 cm. Price \$2.00.

The 27 experiments contained in this book are divided into 12 groups of from 1 to 5 experiments, under the following headings: Molecular Weight from Vapor Density; Vapor Pressure and its Lowering by Solutes; Distillation in Relation to Vapor Pressure; Distribution of Solutes between Phases; Freezing-Point Lowering and Molal Composition; Electrolysis, Transference and Conductance; Rate of Chemical Change; The Equilibrium of Chemical Changes at Constant Temperature; Equilibrium of Chemical Systems in Relation to the Phases Present; Heat Effects Attending Chemical Change; Electromotive Force of Cells; Effect of Temperature on Chemical Equilibrium. Each experiment is carefully organized according to a uniform plan, in which the Principles Involved are first listed, followed in order by an Outline, a description of Apparatus, the detailed Procedure, the required Treatment of Results, and a Discussion of the broader aspects of the experiment and the sources of error.

The individual experiments are, in general, good. This is particularly true, for example, of the study of the equilibrium of hydrogen and iodine at high temperatures, and of several of the experiments on electromotive force. The use of conductivity measurements in following the rate of a

reaction illustrates the advantageous combination of the study of method and principle. It is no doubt the intention that a number of the experiments be used as alternates. The performance of both experiments on vapor density, for example, would disproportionately emphasize this portion of the work. Similarly, it is a question whether experiments on distribution are sufficiently representative or important to justify their utilization in three different assignments. In one case, the endeavor to keep experiments simple and apparatus robust has been carried too far. The experiment on electrolytic conductance, in which the effect is measured of varying the length, concentration, etc., of copper sulfate solution between copper plates in a wooden trough, seems of doubtful value for a student of average intelligence.

In criticizing the book from a more general standpoint it is necessary to bear in mind the author's single intention of emphasizing principles (to large classes with little time). The reviewer is one of those who believe that arrangements as to time and facilities should be made to permit some emphasis of two other important features: (1) the stimulation of the initiative and resourcefulness of the better students in their experimental work, and (2) the study of standard methods, per se, with apparatus good enough to give the feeling that real tools are being used. The work of the present manual consists mainly of set exercises, rather than experiments in the planning or adaptation of which the student takes increasing part as the work progresses. By its sustained carefulness and completeness in this regard, it may fail to assist the instructor in achieving the first of the above objects, and the second of them has been deliberately subordinated. Having made his choice, however, Professor Sherrill has accomplished his purpose with undoubted success.

E. D. EASTMAN

Principles of Chemical Engineering. By WILLIAM H. WALKER, WARREN K. LEWIS and WILLIAM H. McAdams, Professors of Chemical Engineering at the Massachusetts Institute of Technology. McGraw-Hill Book Co., Inc., 370 Seventh Ave., New York; London, 6 and 8 Bouverie Street, E. C. 4; 1923. ix + 637 pp. 156 figs. 23.5 × 15 cm. Price \$5.00.

This book follows the general scheme of dividing industrial chemical processes into a number of basic or "unit" processes, such as flow of heat, distillation, combustion, drying, flow of fluids, etc., and then treating each one of these fundamental operations from a general standpoint without reference to any complete manufacturing process. The underlying, scientific principles are first discussed, then these principles are utilized to explain the phenomena involved and, wherever possible, to develop equations that enable one to predict the result of a change in conditions or to design a piece of equipment for a specified duty. In nearly all cases the use of the equations is well illustrated by the solution of typical prob-

lems founded, for the most part, upon data obtained from actual tests on operating equipment or from undergraduate theses.

The foundation for the quantitative treatment which is accorded to nearly all of the subjects discussed, is well laid in the first chapter, which is devoted to a general exposition of the methods of making industrial calculations. This chapter contains nothing essentially new, but condenses into small space an excellent review of many fundamental laws and clearly shows how they can be pressed into the engineer's service. The quantitative treatment of each subject is usually accompanied by a brief description of the most important standard types of equipment available for commercial use. The limitations and advantages of each are discussed in the light of the general principles previously considered. Notable exceptions to this occur in the cases of "Flow of Heat" and "Flow of Fluids," especially the latter, where one expects some description of fans, pumps, air lifts, etc.

Many of the subjects, such as the flow of heat, combustion, gas, producers, etc., have for some years been included in many of the standard textbooks on mechanical engineering and hydraulics, but from a wholly different viewpoint. For example, in the case of "Flow of Fluids," the quantitative treatment has been generalized. In this book it applies not merely to steam, air and water under the special conditions usually encountered in engineering practice, but to the much greater variety of fluids under many different conditions of pressure and temperature with which the chemical engineer has to deal. Likewise, such subjects as combustion and gas producers are treated from a much more chemical point of view. It is obvious to chemists that the use of molar quantities would introduce considerable simplification.

From the amount of space devoted to filter calculations one is led to believe that commercial filtration has been largely reduced to a mathe-Careful study of the development of the formulas matical basis. reveals that the general equations are, to a large extent, based on assumptions for the validity of which no experimental evidence is adduced. Furthermore, there are so many variables involved in filtration that the constants in the equations are really functions of a number of complex variables and as a result their usefulness is greatly limited. The same criticism applies to the chapter on "Drying," more than 2/3 of which fairly bristles with equations for the design of all kinds of driers under every possible condition. These equations are developed from a few fundamental differential equations involving assumptions as to the mechanism of drying which are not supported by any direct experimental evidence. A few of the final equations are tested on the data obtained from undergraduate theses with satisfactory agreement, but such a test merely serves to show that the equations are satisfactory for the purpose of interpolation under the given conditions.

There is no question as to the desirability of eventually placing all the subject matter of chemical engineering on a mathematical basis, but if this is to be stable it must rest on well-tested principles. This is possible in many cases at the present time, but in others it seems to the reviewer to be decidedly premature.

Chemical engineering covers a rather broad field and naturally the authors have been obliged to limit themselves to a few of the most important subjects. Many chemists and chemical engineers will probably disapprove of the prominence given some subjects, of the scant attention received by others (notably fuels and power) and of the complete omission of many important subjects, such as corrosion, plant control methods, mixing, etc. However, these are points on which no two persons could agree and, on the whole, it may be said that the authors have made a wise selection.

Since it is practically the pioneer in its field this book should receive an enthusiastic welcome from all those who are interested in the application of chemistry (one almost feels constrained to say physics, because the majority of the underlying principles belong more properly in the domain of physics than in that of chemistry) to industry and particularly from those who are concerned with instruction in industrial chemistry and chemical engineering. This is the purpose for which it is primarily intended and it has already proved its worth through having served an extensive apprenticeship as a text, in the form of notes, not only at the Massachusetts Institute of Technology but at several other institutions as well.

One may not agree with all the mathematics, with the arrangement or relative importance given to the various subjects, but one is certainly impressed with the vast amount of quantitative information presented and particularly with the ingenious ways in which well-known scientific principles are applied to the solution of industrial problems.

BARNETT F. DODGE

Lehrbuch der Cellulosechemie (Textbook of Cellulose Chemistry). By Dr. Emil Heuser, Professor of Cellulose Chemistry at the Technical School, Darmstadt. Second edition. Gebrüder Borntraeger, Berlin, 1923. vii + 211 pp. 3 figs. 24.5 × 16 cm. Price \$1.55.

The second edition of this very suggestive and useful monograph, while it includes references to articles on cellulose that have appeared since 1920, shows no great change or development in the author's point of view. The book has been written and rewritten primarily from the standpoint of the organic chemist to whom cellulose is a special type of polyacid alcohol—a specific polysaccharide which is always the same chemical compound no matter what its botanical source. Thus we find the cellulose alcoholates, esters, ethers, as well as oxidation and hydrolysis products of cellulose

discussed from the standpoint of the research chemist as well as that of the technologist with a consistent clarity of expression that merits the highest praise. The circumlocution, which for the past 30 years has haunted monographs on cellulose, and those hopeless labyrinths of detail that demoralized investigators, have disappeared. On the other hand, the interests of the physical chemist and the needs of the technologist who is daily brought into contact with the colloid chemistry of cellulose have been subordinated and at times completely neglected. While the author has done this quite deliberately, realizing the many loose ends that he would encounter in this field, the reviewer regrets that this important phase of cellulose chemistry plays such a minor role in his useful book. Nor does the author always give both sides of a mooted question. As a single example, the work of the physical chemist, Leighton, which argues against compound formation when cellulose is brought into contact with alkali, has received no mention in Heuser's first chapter, whereas the recent (though perhaps less critical) work of the organic chemist, Karrer, which favors the hypothesis of compound formation is duly cited. Hibbert's important critical review of the literature on cellulose, and his subsequent formulation of the constitution of cellulose have not been adequately mentioned and the classical quantitative researches of Irvine and his colleagues at St. Andrews have not been given the place they deserve in Heuser's chapter on "Constitution of Cellulose." In spite of these obvious errors of omission. Heuser's little volume is invaluable to the chemist interested in carbohydrates and to technologists in the many industries in which cellulose serves as a raw material.

Louis E. Wise

An Introduction to the Chemistry of Plant Products. Vol. II. Metabolic Processes. By Paul Haas, D. Sc., Ph.D., University of London, and T. G. Hill, University of London. Longmans, Green and Company, 55 Fifth Avenue, New York; 39 Paternoster Row, London, E. C. 4; Toronto; Bombay, Calcutta and Madras; 1922. viii + 140 pp. 11 figs. 14.5 × 22.5 cm. Price \$2.50 net.

In the third edition of the work under notice the material previously included in one volume has been divided into two parts in order, as has been stated by the authors, to give the more purely physiological aspect of the subject fuller treatment. While, therefore, the first volume is now chiefly restricted to a description of some of the principal chemical constituents of plants, the second one deals more specifically with metabolic processes. The subject matter of the present volume is divided into 6 chapters, which are given the following titles: I. Introduction: The Living Plant; II. The Synthesis of Fats; III. The Synthesis of Carbohydrates; IV. The Synthesis of Proteins; V. Respiration; VI. Growth (including a brief consideration of auximones, hormones and vitamins). Although the changes which take place in living plants were formerly

considered to lie chiefly within the domain of vegetable physiology, and therefore to be more especially of interest to the botanist, it is evident that these metabolic processes are now also actively engaging the attention of the chemist, for it is only by the application of chemical and physical methods that further knowledge can be obtained respecting vital phenomena and their biological significance. It is well known, as the authors have noted, that more than 50 years ago Baeyer formulated the hypothesis that carbon dioxide is split up by the plant into carbon monoxide and oxygen, and that the water is concurrently resolved into its constituent elements. It was further assumed that the carbon monoxide and hydrogen thus produced then combine to yield formaldehyde, which undergoes polymerization and so forms a hexose. These chemical changes which were thus presumed to be comparatively simple have, however, in the meantime been the subject of considerable discussion, with some attending modification of the original views, and for the elucidation of photosynthesis in its fundamental as well as in its broader aspects the most refined methods of chemical investigation have now been brought into requisition. It is to be expected that problems so recondite in character should be attended with many statements which as yet must be regarded as more or less hypothetical or speculative, and also that errors of observation may occur. As an example of the divergence of views respecting the chemical changes effected in biological processes it may be sufficient to call attention to the results obtained by an American investigator1 who has been unable to confirm the statements concerning the reduction of aqueous carbon dioxide to formaldehyde by the action of ultraviolet light and the subsequent polymerization of the aldehyde to hexose sugars.

The work under present consideration is one which will be perused with interest by both chemists and botanists and, although aiming only to present such an account of the various processes and products of plant life as to form a basis for further study, it contains much information of immediate usefulness respecting the existing state of knowledge. The book is well printed and is provided with a very complete index.

F. B. POWER

Clinical Laboratory Methods. By Russell Landram Haden, M.D., Associate Professor of Medicine, University of Kansas, School of Medicine, Kansas City, Kansas. C. V. Mosby Company, St. Louis, Missouri, 1923. 294 pp. 69 figs. and 5 plates. 23.5 × 15.5 cm. Price \$3.75.

Modern diagnostic laboratories are constantly called upon to carry out a considerable variety of procedures. Some of them are in the nature of chemical analyses, both qualitative and quantitative, some are bacteriological, some cytological, and some serological.

¹ Spoehr, This Journal, 45, 1184 (1923).

This book is the equivalent of such note books as are compiled in many laboratories for the benefit of the different workers. No attempt has been made to discuss the procedures or to give alternate methods, beyond indicating the value for each determination found on the average normal subject, or to discuss the interpretation of the results; as the author states in the preface, the book is not a textbook. The reviewer would like to point out that such a book will not enable a chemist to undertake clinical pathological tests, nor will it enable the worker trained in bacteriology and the technique of blood counting to carry out successfully quantitative analyses on blood and urine. The first group of workers would, for instance find difficulty in identifying intestinal protozoa from the charts and tables given, and the clinical pathological worker would almost certainly get into difficulties through ignorance of some of the precautions necessary for insuring purity of reagents, standard solutions, etc., in spite of the precautions described in the twelfth chapter, should he try to carry through chemical analyses.

In the province which the book is intended to cover it is successful. The examinations chosen for presentation are such as are at present of most use in studying patients. None is described that does not have a rather wide application, and few have been omitted that have been proved to have any extensive clinical application. The book, therefore, should be useful for any laboratory as a help in measuring the value of the service which it is prepared to render to the clinician. Whether the methods—particularly the chemical methods described—are those best adapted to each procedure, is a question on which different workers will markedly differ. As was stated in a review of Dr. Haden's book in the British Medical Journal, chemical methods in use are changing so rapidly that probably none of the procedures in use today will continue to be followed 10 years from now; criticism of individual methods is, therefore, of comparatively little value.

It seems to the reviewer that this book will serve very well as the basis for a useful handbook for any clinical pathological laboratory. The successful laboratory will almost inevitably change some of the procedures, omit some and add others; nevertheless, the publication of such a work, if the limitations implied by the statements in the preface are kept in mind, will prove of great value to hospital and commercial clinical pathological laboratories.

ROGER S. HUBBARD

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[Contribution from the Chemical Laboratory of the University of California]

FREE ENERGY OF THE THIOSULFATE ION

By F. Russell Bichowsky¹ Received May 24, 1923

In order to determine the free energy of formation of the thiosulfate ion from its elements, three reactions are suggested as suitable for study.

The first, $S_5^{--} + H_2O = S_2O_3^{--} + 3H_2S$, is known to go, at moderate temperatures, largely in the direction written, and though the reverse reaction has not been described, preliminary experiments show that it takes place to a measurable extent even at 100° . If equilibrium can be reached and can be measured, this reaction gives a new and important means of obtaining not only the free energy of formation of thiosulfate ion but also of sulfur dioxide.²

The second reaction, which appears suitable, is the familiar reaction, $S_2O_3^{--} + H^+ = S + HSO_3^-$. This reaction is known to be reversible, the reverse reaction being one of the usual methods of preparing thiosulfates. However, at acid concentration where the equilibrium is measurable the reaction is very slow at room temperatures, while at higher temperatures difficulties of analysis and the uncertainties of the degree of ionization of the substances involved render this method unsuitable.

The third reaction, $S_2O_3^{--} = S + SO_3^{--}$, is really the same as the second, except that instead of using hydrogen ion to keep the concentration of the sulfite ion low, other means are used to control the concentration of the sulfur or sulfite ion. Biltz³ found that copper reacts with the fused **

¹ National Research Fellow. This research was begun at the Geophysical Laboratory, Washington, D. C., and completed while the writer was National Research Fellow at the University of California.

² By means of the chain of reactions: $4S + HS^- = S_5^- + H^+; H_2S = HS^- + H^+; H_2S = S_7 + H_2; S_5^- + 3H_2O = S_2O_8^- + 3H_2S; SO_2 + H_2O = SO_8^- + 2H^+; S_2O_3^- = S + SO_8^-$, the last of these being the reaction actually measured in this investigation.

³ Biltz, "Laboratory Methods in Inorganic Chemistry," Wiley and Sons, 1909, p. 131.

hydrate of sodium thiosulfate to give cuprous sulfide and sodium sulfite. This reaction is apparently irreversible. It suggests, however, that at high temperatures sodium thiosulfate dissociates into sulfite and sulfur. If this is so, the vapor pressure of sulfur in the equilibrium mixture must be very low, as prolonged heating of either the anhydrous or hydrated sodium thiosulfate in a high vacuum failed to show any distillation of sulfur into the cold parts of the tube, and the reaction mixture, when cooled, failed to give any test for sulfite. At very high temperatures (red heat and above) the reaction, $4\text{Na}_2\text{S}_2\text{O}_3 = 3\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_5$, takes place in preference. It is possible that some metal besides copper might be used, but if the reaction is to be studied in solution, the number of such metals is rather limited.

Moreover, the other alternative, namely, lowering the sulfite concentration by using the thiosulfate of some element whose sulfite is very slightly soluble, would be more satisfactory theoretically, as it would avoid the difficulty of analyzing mixtures of thiosulfates and sulfites, as well as the difficulties of the thermodynamic treatment of such solutions. A number of elements form soluble thiosulfates and insoluble sulfites. The thiosulfates of calcium and barium were chosen for experimental investigation because these elements are divalent, thus eliminating the formation of intermediate ions, they do not readily form thiosulfate complexes, they are not easily hydrolyzed, they exist in only one oxidation stage, and their sulfides are soluble.

Preliminary experiments showed that up to 200° saturated solutions of barium thiosulfate dihydrate which is only slightly soluble, do not dissociate. 2.0 Molar solutions of calcium thiosulfate were partly decomposed into sulfur and calcium sulfite dihydrate, when heated for 4 days at 150°, leaving the solution about 0.4 M. Some hydrogen sulfide and sulfate were formed but no gypsum or anhydrite could be detected in the solid material. The reverse reaction was then tried, that is, calcium thiosulfate dehydrate and sulfur were heated with water for 4 days at 140°. The unaltered sulfur and sulfite were removed and the solution was analyzed: 100 cc. contained 0.01958 mole of calcium ion, 0.01945 mole of thiosulfate ion, 0.0001 mole of sulfide ion, approximately 0.0001 mole of hydrogen ion, and approximately 0.0001 mole of sulfate ion; no sulfite and no polythionate could be detected. It is therefore evident that equilibrium is established at 140° between the separate phases, liquid sulfur, solid calcium thiosulfate dihydrate, and a solution containing only calcium ion and thiosulfate ion at some concentration between 0.4 and 0.19 molar. More careful determinations were, therefore, undertaken.

Preparation of Calcium Thiosulfate Hexahydrate.—Calcium thiosulfate

⁴ Determined microscopically by Mr. Merwin of the Geophysical Laboratory, Washington, D. C.

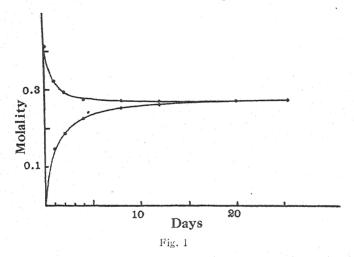
is an extremely soluble salt, a saturated solution at 25° containing 2.28 moles of CaS₂O₃.6H₂O per 1000 g. of solution (new determination). It can readily be prepared in solution by adding a concd. solution of calcium chloride to a cold concd. solution of sodium thiosulfate, when sodium chloride separates. The crystals of calcium thiosulfate can then be fractionally crystallized by adding alcohol, redissolving the precipitate in water and reprecipitating with alcohol. This method works well with small quantities if a trace of alcohol is no objection. For large quantities, the best method is to dissolve 510 g. of crystallized sodium thiosulfate in 465 g. of water, then add, with constant stirring, 350 g. of finely crystallized calcium chloride dihydrate. The temperature of the solution should not rise above 60° during this process. The solution is allowed to stand overnight, the clear solution is decanted through a large filter, and cooled to 0° or -10° and allowed to crystallize. Prepared in this way, the crystals contain only a small amount of sodium chloride as an impurity, from which they can be freed by recrystallization. The solid salt dehydrates rapidly at room temperature, also decomposing into sulfur and sulfite at the same time. In contact with its saturated solution it is stable for several weeks at 25°. At 0° it is apparently indefinitely stable. The 2 M solution is stable up to about 35° and is the most convenient form in which to keep the salt. The solutions used in this investigation were free from excess of calcium and contained less than 0.1% of sodium chloride.

Calcium Sulfite.—The dihydrate was prepared (1) by precipitation of fresh sodium bisulfite with calcium chloride, (2) by recrystallization of commercial calcium sulfite from a solution of sulfurous acid, (3) by partial oxidation of calcium thiosulfate with hydrogen peroxide in alkaline solution (a new reaction), (4) by thermal decomposition of solutions of calcium thiosulfate. These samples varied strikingly in crystalline habit, but had nearly the same refractive index, and no difference in behavior was noted among them. The material used in the final experiments was all prepared by Method 1. Above temperatures somewhere near 160° the dihydrate is unstable in contact with water, presumably forming the semi-hydrate, CaSO₃.1/2H₂O, analogous to CaSO₄.1/2H₂O.

The sulfur used was the common purified substance.

Equilibrium Measurements.—Two sets of sealed Pyrex tubes were made up, each of the first containing about 15 cc. of M calcium thiosulfate solution to which a little powdered sulfur and calcium sulfite dihydrate were added; each of the second, 15 cc. of water and an excess of sulfur and calcium sulfite dihydrate. These were heated side by side in an air thermostat, constant to 0.5° of the temperature desired. From time to time one from each set was withdrawn, cooled, filtered through a dry filter into a weighed flask containing a few drops of a solution of cadmium

acetate to precipitate any hydrogen sulfide present. The flask was then weighed again, and its contents filtered through a dry filter to remove cadmium sulfide. The precipitate was washed until the washings did not affect the titer and the filtrate was titrated with 0.1 N iodine solution; weighed burets were used. If equilibrium were reached the concentration of both tubes should be the same. In the case where special care was taken, as in the experiment at 141°, the values from above and below did not differ by 0.1%, and there is apparently no reason why this accuracy should not be reached, if needed, at any temperature. At 174° equilibrium was not reached, the titer of the tubes starting with the thiosulfate side remaining constant at 0.118 M per 1000 g. of solution, and those from the water side slowly changing at a concentration of about 0.158 M per 1000 g. solutions, even after 2 weeks' heating. Microscopic examination showed that in the first case the solid phase was not calcium sulfite



dihydrate, but presumably the semihydrate. In the tubes containing water the solid material was largely the dihydrate with some semihydrate present. An accident prevented the completion of the run at 120° and the results are not accurate. The results of a typical run are presented in Fig. 1.

At temperatures below 110° the reaction was too slow to allow this method to be used. So, instead of starting with pure water or a concentrated solution of thiosulfate, solutions of known strength, say 1.2, 1.00, 0.80, 0.60 M were prepared and heated in the presence of calcium sulfite dihydrate and sulfur in sealed Pyrex bulbs in a vapor bath. Samples were withdrawn after a week and analyzed, and it was noted whether the strength of the calcium thiosulfate had decreased or increased. Thus it could be determined that the equilibrium concentration lay between, say,

1.00 and 0.80. By making up a new set of tubes with concentrations of 1.00, 0.95, 0.90, 0.85, 0.80, M the process could be repeated and the equilibrium limits narrowed still more. Table I gives the results of one such run.⁵ Final values for the equilibrium concentrations are given in Table II, where Line I gives the temperature, Line 2, the concentration in moles per 1000 g. of water, and Line 3, the form of sulfur stable at the temperature in question.

TABLE I

	Sample Eq	UILIBRIUM DET	TERMINATION	
Original concentration	After 6 days	After 14 days	After 30 days	After 50 days
1.427	1.17	1.12		
1.142	1.12	1.076	1.026	1.025
0.950	0.964	0.990	1.006	1.010
0.660	0.713	0.757		
0.478	0.598	0.695		

TABLE II

Equilibrium Concentrations

Temp., °C	141	122	110	100	79.8
Conen	0.2665	0.417	0.618	0.713	1.120
Form of sulfur	$S_{\lambda\mu}$	$S_{\lambda\mu}$	$S_{\mathbf{m}}$	$S_{\mathbf{m}}$	$S_{\mathbf{r}}$

In order to use these equilibrium data to calculate the free-energy change at the standard temperature and concentration it is necessary to know the heat of the reaction, the heat of dilution of these concentrated solutions, the heat capacity of all substances involved and the free energy of dilution of the thiosulfate solution.

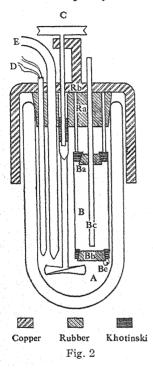
The Heat of Reaction.—No direct determination of this quantity was available, and though it may be calculated from the equilibrium measurements themselves, the calculation is so involved in this case that it was thought advisable to determine this factor calorimetrically. In theory this may readily be done by treating in a calorimeter a solution of calcium thiosulfate with an excess of acid and then, under identical conditions, an equivalent amount of calcium sulfite dehydrate with the same amount of the same acid. The chief chemical difficulty lies in the fact that the sulfur formed by the action of acids on thiosulfate solutions is not rhombic sulfur but a mixture of S_{λ} and S_{μ} . Under the conditions of these experiments the change of these substances into rhombic sulfur is slow and the heat involved in that process must be allowed for. A rough approximation

⁵ It will be noted that the rate of the reactions by which thiosulfate is formed is quite different (being between two different phases) from the rate at which it decomposes, though, of course, the slope of the two curves in Fig. 1 must be equal at equilibrium. At any given time short of equilibrium the one reaction is thrice as far from equilibrium as the other.

⁶ Brownlee, This Journal, 29, 1032 (1907).

of the heat involved may be made from existing data. Under the conditions of the experiments the value estimated was 110 cal. per mole. Fortunately, in one case, the sulfur could be isolated, washed, and treated with ammonium hydroxide in the calorimeter and this value determined directly. The value found was 200 calories per mole.

The apparatus used in our calorimetric experiments, except those in the heat capacity of calcium sulfite dihydrate, is shown in Fig. 2. The



calorimeter was submerged up to the stopper in a large, stirred water-bath, the heavy copper parts serving to keep the top at approximately the temperature of the bath. At the beginning of the experiment, the stopper Ba and appurtenances were inverted, the stopper Ba adjusted, and the vessel B filled with a known weight of 1:1 hydrochloric acid. Stopper Bb was then adjusted, the Dewar flask A filled with a known weight of water and of calcium sulfite or of calcium thiosulfate solution of equivalent strength. The stopper Ba and appurtenances were then put in place. The thermel, E (in most cases a 15 junction thermel belonging to Dr. White) was inserted, the calorimeter placed in the bath, and the run begun,8 using all the usual precautions of the fore period and stirring described in Dr. White's paper.9 At the moment of mixing, stirring was stopped and the stoppers Ba and Bb were pushed out by means of rod Bc, the stopper Bb swinging back against the wall of the Dewar flask on the platinum wire hinge Be. Stirring was then started and the run com-

pleted in the usual manner. The heat capacity was determined electrically, using the heater D. The current and the voltage were read on a White double potentiometer, the time being controlled by a very accurate interval switch belonging to Dr. White. The final values for the two reactions are: for Reaction (1), 0.0638 mole of CaS_2O_3 in 302 g. of soln. +64.02 g. of 1:1 HCl solution = 205.51 calories of heat absorbed. The sulfur formed

⁷ Lewis and Randall, "The Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Co., 1923, p. 532. The nomenclature of these authors is adopted throughout this paper.

⁸ All of the calorimetric determinations except those starred were carried out in Dr. White's laboratory in the Geophysical Laboratory in Washington, D. C., often with Dr. White's personal assistance. I wish here to express my gratitude to Dr. White for these many courtesies.

⁹ White, This Journal, 40, 1872 (1918).

contained 10.1% S_u. (2)* 0.06374 mole of CaS₂O₃ in 302 g, of solution + 63.99 g. of 1:1 HCl = 206.60 calories of heat absorbed. In this run the calorimeter was washed, 0.5 M ammonium hydroxide added to the vessel B and water added to the vessel A. When these were mixed there was a quick evolution of heat, followed by a slow evolution of heat amounting to about 10 calories, or 200 calories per mole of sulfur present. Calculation gives 110 calories per mole for the reaction $S_{\lambda\mu} = S_r$, on the assumption that the sulfur is "hardened" before the run began, and 365 calories on the assumption that it is not. (3) 0.06382 mole of CaSO₃.2H₂O (10.381 g.) and 290.1 g. of H₂O + 64.00 g. of 1:1 HCl solution = 212.5 calories of heat evolved. (4) 0.0639 mole of CaSO₃.2H₂O and 290.3 g. of water + 64.05 g. of 1:1 HCl solution = 212.2 calories of heat evolved. (5)* Another sample of calcium sulfite dihydrate calculated to the same weight gave 215.0 cal. We shall take for the reaction CaS2O3 (0.2127 mole per 1000 g. of soln.) = $CaSO_3.2H_2O + S_r$, $\Delta H = -6300$. believed that the total error due to heat losses, etc., does not amount to over 10 calories per mole, but due to the slowness of the reaction involving thiosulfate and sulfur the error in the total heat of reaction may be many times this, say, 1000 calories per mole.

Heat of Dilution.—Using the same apparatus, the heats of the following reactions were determined. (1) (1 mole of CaS₂O₃ in 33.50 moles of H₂O) + (197.4 moles of H_2O) = (1 mole of CaS_2O_3 in 230.4 moles of H_2O); $\Delta H = 408.5 \text{ cal.}$ (2)* (1 mole of CaS₂O₃ in 33.4 moles of H₂O) + 197 moles of $H_2O = (1 \text{ mole of } CaS_2O_3 \text{ in } 230.4 \text{ moles of } H_2O)$; $\Delta H = 407.9$ (3) (1 mole of CaS_2O_3 in 33.5 moles of H_2O) + (0.734 moles of CaS_2O_3 in 164.8 moles of H_2O) = (1.724 moles of CaS_2O_3 in 198.3 moles of H_2O); $\Delta H = 177.5 \text{ cal.}$ (4)* (1 mole of CaS₂O₃ in 33.5 moles H₂O) + (320 moles of H_2O) = (1 mole CaS_2O_3 in 353.5 moles of H_2O); $\Delta H = 353$ cal. It would have been better to carry out measurements in even more dilute solutions but the advantage of this was not realized until the apparatus was no longer available. Reaction 3 can be combined with Reaction 1 giving Reaction 3a, that is, (1 mole of CaS₂O₃ in 33.5 moles of water) + (83 moles of H_2O) = (1 mole of CaS_2O_3 in 116 moles of H_2O); $\Delta H = 274$ cal. It will be noted that of Equations 1, 3a and 4, each gives the heat effect of adding x moles of water to a thiosulfate solution of the same strength. It happens that the data for these experiments fall on an hyperbola whose equation is $\Delta H = \frac{N'_1}{0.163 + 0.00168 N'_1}$ where N'_1 is the number of moles of water added to 1 mole of calcium thiosulfate dissolved in 33.5 moles of H₂O. Changing units we obtain $^6\Delta H = \frac{N_1 - c}{E_1 + BN_1}$ where N_1 is the number of moles of water in the final solution to 1 mole of calcium thiosulfate. E = 0.107; c = 33.5 and b = 0.00168. Now $\frac{\partial H}{\partial N_1}$ = $\overline{L_1}$ the partial molal heat content of the water of the solution and $N_1 \frac{\partial \overline{L_1}}{\partial N_1} = \partial \overline{L_2}$. Or, carrying out the indicated transformation, $\overline{L_1} = \frac{E + bc}{(E + bN_1)^2}$ and $\overline{L_2} = \frac{E + bc}{b} \left\{ \frac{E + 2bN_1}{(E + bN_1)^2} \right\}$. Values of $\overline{L_1}$ and $\overline{L_2}$ for the mol ratio N_1 given in Col. 1 are tabulated in Table III.

TABLE III

HEAT CONTENT OF SOLUTION

N_1	208	141.3	89.8	77.9	49.5
ī.,	0.785	1.38	2.45	2.88	4.52
L_2	-376	-487	-597	-635	-735

Specific Heat of Solutions of Calcium Thiosulfate.—Incidental to determining the heat of dilution, the specific heats of the various concentrations of calcium thiosulfate were determined. The values found were 0.704, 0.769, 0.840, 0.918, 0.954 for solutions whose concentrations were 1.750, 1.3234, 0.888, 0.447 and 0.213 M, respectively. Using the method of intercepts, the values of \overline{c}_{p_1} and \overline{c}_{p_2} were determined. These values for the concentrations used in the equilibrium experiments are given in Table IV, Lines 2 and 3, respectively. Line 1 gives the concentration in moles per 1000 g. of water.

TABLE IV

Partial Molal Heat Capacity 0.1625 0.2665 0.393 0.618

Concil	0.1020	0.2000	0.585	0.019	0.713	1.120
\overline{c}_{p1}	18.00	17.99	17.98	1795	17.90	17.70
\overline{C}_{p2}	-3.4	-3.4	-3.3	-3.2	-3.1	-2.6

Heat Capacity of Calcium Sulfite Dihydrate.—A preliminary estimate of the change of heat capacity of the equilibrium reaction based on known data and a value for $c_p/\text{CaSO}_3.2\text{H}_2\text{O}$ based on Kopp's law showed that the Δc_p term in the free-energy equation would have quite exceptional importance. No value of the specific heat of calcium sulfite dihydrate, $\text{CaSO}_3.2\text{H}_2\text{O}$, being available in the literature, determinations were undertaken, using a simple calorimeter, and the drop method. Quartz was used as a comparison substance. Using two different samples of calcium sulfite, almost identical values were obtained, namely 0.274 and 0.273 calories per g. or 42.7 calories per mole. Kopp's law gives 41.1 calories per mole.

Free Energy of Dilution of Solutions of Calcium Thiosulfate.—In order to obtain the free energy of dilution of solutions of calcium thiosulfate, several series of freezing-point curves were made. The set in which most confidence can be placed was made with an apparatus similar to that described by Rodebush, 10 and Rodebush's original 4-junction thermel.

¹⁰ Rodebush, This Journal, 40, 1204 (1918).

Values of the concentration in moles per 1000 g. of solution and Δt are: m = 1.260, $\Delta t = -3.96$; m = 0.810, $\Delta t = -2.106$; m = 0.578, $\Delta t =$ -1.414; m = 0.264, $\Delta t = -0.623$; m = 0.0674, $\Delta t = -0.160$. Besides these, the following values at lower concentrations appear to possess some meaning: m = 0.02045, $\Delta t = -0.0482$; m = 0.0106, $\Delta t = -0.0282$; m = 0.00553, $\Delta t = 0.0156$. As far as these determinations go, the activity coefficient seems to be about that found by Lewis and Randall for bivalent sulfates. The best estimate appears to make the activity coefficient 0.40 at 0.01 M. Using this value as a basis, and following the methods of calculation used by Lewis and Randall, the values for γ , the activity coefficient at 25° of solutions of calcium thiosulfate for the equilibrium concentrations, were obtained. The heat capacity and the heat of dilution and its change with concentration were not neglected in this calculation. $m = 0.01, \gamma = 0.40; m = 0.20, \gamma = 0.165; m = 0.163,$ $\gamma = 0.149$; m = 0.2665, $\gamma = 0.127$; m = 0.393, $\gamma = 0.113$; m = 0.618, $\gamma = 0.0995$; m = 0.713, $\gamma = 0.0972$; m = 1.117, $\gamma = 0.0964$.

With these data at hand, it is now possible to calculate ΔF_{298} for the reaction CaSO₃.2H₂O + S_r = CaS₂O₃ aq. + 2H₂O, directly from the equilibrium measurements. It is convenient, however, instead, to modify the usual procedure somewhat, and calculate the activity of each of the solutions employed at the temperature of equilibrium. This is the true equilibrium constant of the actual reaction at that temperature.

The results for the logarithm of the equilibrium constant are: T $= 414, \log K = -2.971; T = 393, \log K = -2.630; T = 383, \log K =$ -2.334; T = 373, $\log K = -2.221$; T = 352, $\log K = -1.881$. This is the equilibrium constant for the reaction in which the sulfur is in the form stable at the temperature of the measurement, that is, the form given in Table I, Col. 4. The equilibrium constant for the reaction CaSO3.- $2H_2O + S_r = CaS_2O_3$ aq. $+ 2H_2O$ is slightly different from this. This correction may be calculated from the free energies of the various reactions: $S_r = S_{\lambda u}$, $\Delta F_{447} = -90$, $\Delta F_{414} = -35$, $\Delta F_{398} = -20$; $S_r = S_m$, $\Delta F_{383} = -2$, $\Delta F_{373} = -1$, as given by Lewis and Randall. Using the data on the heat capacity of H₂O and S_r given by Lewis and Randall, 12 together with the data obtained in this paper, the change of heat content for this reaction is: $\Delta H = -1945 - 14.02T - 0.00235T^2$ or $-RI \ln K$ $= -1945 + 14.02T \ln T + 0.00235T^2 + IT$. From this equation it may be calculated for T = 414, I = -67.1, T = 393, I = -67.8; T = -67.8383, I = -69.7; T = 373, I = -69.7; T = 353, I = -69.9. There appears to be a trend in the values of I, due presumably to a faulty value of the heat of reaction and also in part to the unsatisfactory freezing-point data. The best value appears to be I = -68.6. For the reaction S.

¹¹ Ref. 7, p. 532.

¹² Ref. 7, pp. 102, 531.

+ CaSO_{3.2}H₂O = CaS₂O₃ (M) + 2H₂O, therefore, ΔF° = 1310 calories. The error here is probably not over 300 calories and might easily be decreased, given better thermal and activity data.

Solubility of Calcium Sulfite Dihydrate.—The solubility of this substance has been determined by Weisberg¹³ and by van der Linden.¹⁴ Their results are 0.057 g. per liter at 18° and 0.065 g. per liter at 25°, respectively. However, it is difficult to prepare calcium sulfite dihydrate free from gypsum, the presence of which would affect the solubility very greatly. Van der Linden notes that his sulfite was not free from sulfate and hence presumably contained gypsum. At any event, the solubilities determined above are not consistent with the solubility of calcium sulfite dihydrate in a solution saturated with gypsum as determined by van der Linden, namely, 0.032 g. per liter. A series of determinations was therefore undertaken with various samples of calcium sulfite, in which the solution was saturated at 25° and titrated with 0.001 N iodine solution. Contrary to the common opinion, even more dilute solutions of iodine can be used without an abnormal blank correction, provided the solution is kept 0.1 N in iodide ion. The sulfite used was prepared, (1) by precipitating the salt from solutions of calcium chloride by the addition of sulfur dioxide and sodium hydroxide simultaneously, (2) by dissolving calcium sulfite dihydrate in a pure solution of sulfurous acid and precipitating the salt by boiling off the sulfur dioxide in a vacuum, (3) by washing the commercial salt with air-free distilled water. None of these samples was quite free from sulfate. The values for the solubility obtained were, respectively. 0.000202, 0.000107, 0.000087 mole per liter. The solubility of Samples 1, 3, and the commercial salt in the presence of solid gypsum were 0.0000371, 0.0000367, 0.0000372 mole per liter or 0.029 g. per liter, agreeing closely with the value of van der Linden. Taking 0.000037 as the final value and applying the principle of ionic strength,7 the mean activity of the sulfite and calcium ions in a saturated solution of calcium sulfite dihydrate at 25° is 0.000261; that is, for the reaction $Ca^{++} + SO_3^{--} + 2H_2O =$ CaSO₃.2H₂O, $\Delta F_{238}^{\circ} = -9740$ or, adding $\Delta F_{238}^{\circ} = -8430$ for the reaction $SO_3^{--} + S_r = S_2O_3^{--}$. Now, Lewis and Randall give for the free energy of formation of the sulfite ion, $\Delta F_{298}^{\circ} = -116,680$. Therefore, the free energy of formation of the thiosulfate ion in solution of unit activity is -125110 calories.

Summary

A complete thermodynamic study has been made of the reaction, $S + CaSO_3.2H_2O = CaS_2O_3$ aq. $+ 2H_2O$. This reaction has been proved to be reversible and the equilibrium constant has been measured at various temperatures. The heat of the reaction has been determined experi

¹³ Weisberg, Bull. soc. chim., [3] 15, 1097.

¹⁴ Van der Linden, Arch. Sukerind., 24, 1113 (1916).

mentally as have the specific heat, freezing point and heat of dilution of solutions of calcium thiosulfate of various strengths. The solubility of calcium sulfite dihydrate and its specific heat have also been measured. Using these and other data, the free energy of formation, ΔF_{208} ° of the thiosulfate ion has been calculated to be —125,110 calories.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE CATALYTIC COMBINATION OF ETHYLENE AND HYDROGEN IN THE PRESENCE OF METALLIC COPPER II. MEASUREMENTS OF REACTION VELOCITY AT 150°, 200° AND 250°

By Robert N. Pease Received May 31, 1923

In a recent paper¹ the author has recorded results which indicate that the combination of ethylene and hydrogen in the presence of copper at 0° and 20° is, in its first stages, approximately monomolecular with respect to hydrogen, while ethylene in excess acts as an inhibitor. Grassi² has studied this reaction to some extent at temperatures between 150° and 275° and reports that in this region the reaction is bimolecular, as would be expected from the chemical equation. Grassi also found that the temperature coefficient between 150° and 275° was very small and decreased with rising temperature whereas between 0° and 20°, the author found the temperature coefficient to be in the neighborhood of 1.6 per 10°, which is of the same order as that for many uncatalyzed reactions. These marked differences in the characteristics of the reaction in the two temperature regions made it important to repeat a part of Grassi's work, especially as this investigator carried his determinations over only a small fraction of the total reaction.

The apparatus and method were the same as those used in the previous determinations at 0° and 20°, except that the temperature was maintained by means of an electrically heated air-bath. The copper catalyst in the state in which it was used for the runs at the lower temperature was much too active for use in the neighborhood of 200°. Partial de-activation was accomplished by heating it to 500-550° in a vacuum. During this treatment, the catalyst shrank about 15% of its original apparent volume and turned from a dirty red-brown to a salmon pink.

Reaction Velocity at 200°

The catalyst in the latter stage of activity was used for a series of runs at 200°. The results of this series, which are shown graphically in Figs. 1 and 2, indicate that the reaction is not exactly bimolecular as Grassi

¹ Pease, This Journal, 45, 1196 (1923).

² Grassi, Nuovo cimento, [6] 11, 147 (1916).

states, though it approximates to this. For a bimolecular reaction, Curve I for the 50% mixture should lie to the left of the other two, as it does, in accordance with the principle that for a bimolecular reaction the velocity is a maximum with such a mixture. The other two curves, corresponding to 2:1 mixtures, should coincide. Actually, the velocity appears to be somewhat greater when hydrogen is in excess.

The decrease in pressure when hydrogen is in excess, is probably due in part to the solution of hydrogen in the copper. It is certain that the copper was able to take up some hydrogen, as was shown by measurements at 200°

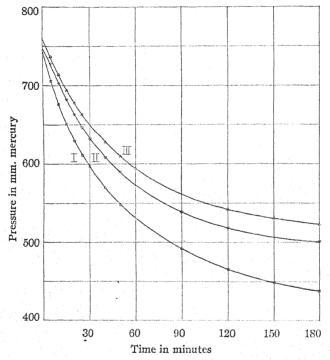


Fig. 1.—Reaction velocity at 200°, with initial pressure of 1 atmosphere. Curve I, 50% mixture, Run 105,[\bigcirc]; Curve II, $2H_2-1C_2H_4$, Run 110,[\triangledown]; Curve III, $1H_2-2C_2H_4$, Run 108,[\triangle]

of pressure against volume with pure hydrogen. After each addition of gas there was a slow "drift" in the pressure, lasting sometimes for hours, and the total hydrogen in the bulb at any pressure was distinctly greater than that of either helium or ethylene. (These two gases gave the same results within experimental error, indicating that only minimal amounts of ethylene are adsorbed.) While it is impossible to state with certainty that this hydrogen was dissolved and not adsorbed, everything points to this. Previous heat treatments had caused marked decreases in the ad-

sorption at 0° so that even at this temperature only a small adsorption was to be expected, and at 200° this must have been reduced to negligible proportions, if adsorption decreases with increasing temperature as is usually assumed. Nevertheless at 0.5 atmosphere and 200° , 1.0 cc. of hydrogen was taken up. This is as much as the same catalyst in a tremendously more active state took up at 0° . Furthermore, if this hydrogen is all adsorbed, it is adsorbed in many times greater quantity than ethylene.

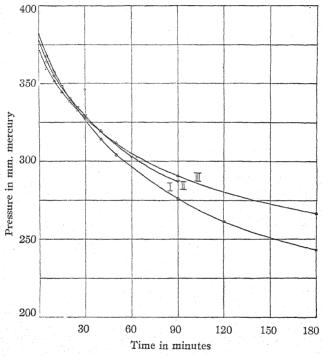


Fig. 2.—Reaction velocity at 200°, with initial pressure of 0.5 atmosphere. Curve I, 50% mixture, Run 106,[\odot]; Curve II, $2H_2 - 1C_2H_4$, Run 111,[∇]; Curve III, $1H_2 - 2C_2H_4$, Run 109,[\triangle]

This would lead one to expect a marked influence on the reaction velocity, when none is found.

Reaction-velocity measurements were carried out with 50% mixtures and mixtures containing 2 volumes of one gas to 1 volume of the other, each at initial pressures of 0.5 and 1 atmospheres. To determine how the reaction velocity varies with the hydrogen and ethylene concentrations, the decreases in pressure in millimeters of mercury from the 5th to the 15th minute (ΔP) have been compared with the initial volumes of each of the gases in the bulb. Thus, in one experiment there were 4.14 cc. of hydrogen and 8.10 cc. of ethylene, while ΔP was 15.0 mm. In another

there were 8.33 cc. of hydrogen and 4.17 cc. of ethylene, while ΔP was 16.5 mm. Again, in one experiment there were 8.52 cc. of hydrogen and 16.65 cc. of ethylene, while ΔP was 42.0 mm. In another, there were 16.65 cc. of hydrogen and 8.33 cc. of ethylene, while ΔP was 46.0 mm. It is seen that for the same amounts of 2:1 mixtures, the velocity is nearly the same whether hydrogen or ethylene is in excess, although an excess of hydrogen seems to correspond to a slightly greater velocity, as already mentioned. A comparison of reaction velocities when the amount of one gas is the same and the other is varied indicates, however, that a simple proportionality does not exist between gas concentration and reaction velocity. Thus, in two of the experiments, there were 8.10 cc. and 8.33 cc. of ethylene, respectively, while the volumes of hydrogen were 4.14 cc. and 16.65 cc. The corresponding reaction velocities were 15.5 mm. and 46.0 mm. The volumes of hydrogen stand in the ratio of 1:4.0. while the reaction velocities stand in the ratio of 1:3.0. In two other experiments the volumes of hydrogen were 8.33 cc. and 8.52 cc., respectively, while the volumes of ethylene were 4.17 cc. and 16.65 cc. The corresponding reaction velocities were 16.5 mm, and 42.0 mm. The volumes of ethylene stand in the ratio of 1:4.0 while the ratio of reaction velocities is 1:2.5. If it is assumed that the relation between reaction velocity and concentration can be expressed by $(dp/dt) = k \cdot V_{Ha}^{a} \cdot V_{Collar}^{b}$ these relationships would give a = 0.80 and b = 0.66. The reaction velocity seems to vary not as the first power of the concentrations but as the 0.8 power of the hydrogen concentration and the 0.66 power of the ethylene concentration. If it is assumed that reaction velocity is directly proportional to the product of the amounts of the two gases adsorbed, the adsorptions of the gases should vary with these same fractional exponents of the pressure.

The results of calculations of the velocity constant, k in the equation $(\mathrm{d}p/\mathrm{d}t) = k \cdot V_{\mathrm{H}_2}^{0.80} \cdot V_{\mathrm{C};\mathrm{H}_2}^{0.86}$, are given in Table I. The values of ΔP , the decrease in pressure from the 5th to the 15th minute, were substituted for $\mathrm{d}p/\mathrm{d}t$ and the initial volumes of hydrogen and ethylene for V_{H_2} and $V_{\mathrm{C};\mathrm{H}_2}$. Values of K were then calculated. $k = \Delta P/(V_{\mathrm{H}_2}^{0.8} \cdot V_{\mathrm{C};\mathrm{H}_2}^{0.66})$. It is seen that the constants agree reasonably well.

TABLE I

	THE VELOCI	TY CONST	ant at 20	0°		
Run No. 1	05 106	108	109	110 1:	11 11	2
$V_{\mathrm{H_2}}$	2.31 6.38	8.52	4.14 16	6.65 8	.33 12	.48
$V_{C_2H_4}$	2.31 6.37	16.65	8.10	3.33 4	.17 12	.57
$\Delta P \dots 5$	4.5 20.0	42.0 1	5.0 46			.0
<i>K</i>	1.4 1.3	1.2	1.2 1	1.2 1	.2 1	.3

It has already been mentioned that no measurable amount of ethylene is adsorbed at 200° and that it is very doubtful if hydrogen is, either.

Under these circumstances, it is not surprising to find that the reaction approximates more nearly to what one would expect, namely, a bimolecular reaction. The reaction at 0° was found to be approximately monomolecular with respect to hydrogen and to be partially inhibited by ethylene. This latter could be traced to the marked adsorption of ethylene by the catalyst. In the absence of such marked adsorption at 200°, no such effect would be expected and none is found.

Temperature Coefficient

Grassi² found that for equal initial concentrations (not pressures) of 50% mixtures, the initial decreases in pressure in each 10-minute interval

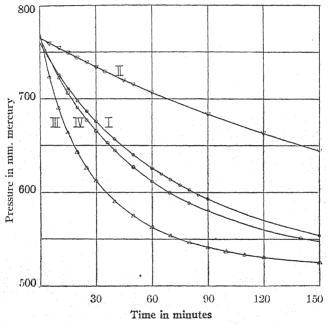


Fig. 3.—Reaction velocity at 150°, 200° and 250°, initial pressure of 1 atmosphere.—Mixture of $2C_2H_4-1H_2$. Curve I, velocity at 200°, Run 116,[\bigcirc]; Curve II, velocity at 150°, Run 117,[\bigcirc]; Curve III, velocity at 250°, Run 118,[\triangle]; Curve IV, velocity at 200°, Run 119,[\bigcirc]

at 150°, 200°, 250°, and 275° were 2.2, 10.7, 12.8, and 14.0 mm., respectively. When these are corrected for temperature, and 200° is taken as the standard, they become 2.4, 10.7, 11.6, 12.1 mm. Since the concentrations are the same, the velocity constants are directly proportional to the above corrected pressure decreases. These correspond to a very small and continuously decreasing temperature coefficient.

For comparison with Grassi's results, the author measured the reaction velocity at 150°, 200° and 250°. In these experiments a mixture of 1

volume of hydrogen to 2 volumes of ethylene was used, as it was thought that there would be less interference due to solution of hydrogen with such a mixture. The results of these measurements are shown graphically in Fig. 3. In Table II are given values of k calculated by the same relation as before, namely, $k = \Delta P/(V_{\rm H_2}^{0.8}, V_{\rm C_2H_4}^{0.66})$. The values of ΔP have been corrected for temperature. The volumes are those at 0° and 760 mm.

 $\label{table II}$ Reaction Velocity at 150°, 200° and 250°

	Temp.				•			
Run No.	۰c.	$V_{ m H2}$	V_{G2H4}	ΔP	k	$\Delta k/_{10}$ °	$\Delta P(\text{Grassi})$	$\Delta k/_{10}$ °
116	200	8.40	16.79	36.5	1.05 $)$	1.31	10.7	1.35
117	150	9.30	18.60	11.2	$0.27 \int$	1.91	$2.4\int$	1.00
118	250	7.67	15.35	53.8	1.74	1.15	11.6	1.02
119	200	8.32	16.63	30.0	0.85∫	1,10	(10.7)	1.02

Unfortunately, there was a noticeable decrease in activity during these runs. This has been taken into account in calculating temperature coefficients.

For comparison, the values of ΔP from Grassi's results are given. These correspond directly to velocity constants, since the gas concentrations were made the same at the different temperatures. It will be seen that between 150° and 200°, the temperature coefficients of reaction velocity calculated from the two sets of results are in good agreement (1.31 and 1.35). Between 200° and 250°, the author's results give a distinctly higher coefficient than do those of Grassi, (1.15 and 1.02). Both sets agree, however, in assigning a very small and continuously decreasing coefficient to the reaction. The decrease in temperature coefficient between the 150–200° regions and the 200–250° regions is abnormally large even with the authors'

values. On the basis of the Arrhenius equation, $\log \frac{k_2}{k_1} = \frac{A}{4.57} \cdot \frac{T_2 - T_1}{T_1 \cdot T_2}$, there is a normal decrease with increasing temperature if A, the so-called "heat of activation," is regarded as constant. The observed values of k are not in agreement with this assumption, however, the calculated values of A being 10800 cal. between 150° and 200° and 7000 cal. between 200° and 250°. As an explanation of the anomalous result just mentioned, the decrease in the adsorptive power of the contact mass with increasing temperature suggests itself. The active masses in a contact catalytic action are functions of the amounts of reactants adsorbed. In comparing reaction rates at two temperatures, the comparison should therefore be made at such gaseous concentrations that equal amounts of reactants are adsorbed at the two temperatures. Actually, comparisons are made at equal gaseous concentrations, corresponding to continuously decreasing adsorptions, or surface concentrations, with increasing temperature. This leads to temperature coefficients (and heats of activation) smaller

than the true ones corresponding to the reaction on the surface and continuously decreasing, unless the adsorption is a linear function of the temperature. The observed temperature coefficient is composite of two effects, namely, the true positive coefficient of the surface action and the negative coefficient of adsorption. In the present case the adsorptions at the temperatures in question were not measurable in the case of ethylene and are of doubtful significance in the case of hydrogen, so that no such correction can be made. That the adsorption of ethylene by copper does decrease markedly through a part of the temperature region is shown by the results of Taylor and Burns,³ who found that the adsorption at 1 atmosphere on a particular sample of copper was 0.65 cc. at 110° and not measurable at 218°. Experiments are at present in progress to determine the temperature coefficients of adsorption of ethylene and hydrogen on active copper between 0° and 200°.

Although the absolute reaction velocities in the experiments at 0° and 20° already reported are not directly comparable with those just given because of the enormous difference in catalytic activity, it might be expected that the temperature coefficients of reaction velocity (and the heats of activation) might be compared. The velocity constants at 0° and 20° were 0.50 and 1.32 in the particular units chosen, leading to a temperature coefficient of 1.62 per 10° and a heat of activation of 7700 cal., a value which lies between the two obtained at the higher temperatures (10,800 cal. and 7000 cal.). Since the adsorption of hydrogen at 0° and 20°, upon which the reaction appears to depend in this region, was the same, one would have expected that the temperature coefficient and heat of activation in this temperature region would have been the true one for the surface action on the basis of the argument already given. In this case a value for the heat of activation considerably larger than that at the higher temperature was to have been expected instead of an intermediate value. Perhaps further discussion may best be postponed until more results have been accumulated. It is of interest, however, to find that the heats of activation for the reaction in the presence of the copper catalyst in two such different states of activity are of the same order.

This investigation was carried out with the aid of a National Research Fellowship in the Laboratory of Physical Chemistry, Princeton University.

Summary

Measurements of the velocity of combination of hydrogen and ethylene in the presence of copper at 150°, 200° and 250° have shown that in this temperature region the reaction is more nearly bimolecular, in contrast to the combination at 0°, at which temperature the reaction is approximately monomolecular with respect to hydrogen and inhibited partially by excess

^{*} Taylor and Burns, This Journal, 43, 1273 (1921).

of ethylene. The more nearly normal character of the reaction at the higher temperatures is believed to be due to the fact that under these circumstances the reacting gases are not measurably adsorbed by the catalyst. The temperature coefficient is much smaller at the higher temperature and is decreasing. By taking into account the decrease of adsorption with rise in temperature as well as the normal increase in velocity of the surface reaction, these facts have been accounted for qualitatively.

University, Virginia

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

THE KINETICS OF THE CONVERSION OF CREATINE INTO CREATININE IN HYDROCHLORIC ACID SOLUTIONS

By Graham Edgar and R. A. Wakefield Received June 4, 1923

Introduction

The literature contains numerous references to the conversion of creatine into creatinine in the presence of acid catalysts. Practically all of these investigations have either been purely qualitative in nature, or have been concerned with determining the conditions under which the reaction goes to completion, in order to permit the quantitative estimation of creatine (as creatinine) by the colorimetric method of Folin.¹

The reversible reaction

$$H-N = C \begin{cases} NH_2 \\ N-CH_2COOH \end{cases} \longrightarrow H-N = C \begin{cases} NH-C = O \\ N-CH_2 \\ CH_3 \end{cases}$$

$$Creatine \qquad Creatinine$$

$$CT = O \\ CH_3 \\ CT = O \\ CH_3 \\ CT = O$$

$$CT = O \\ CT = O$$

is of great interest in biochemistry, as it occurs in the normal and abnormal processes of the metabolism; it is also of interest from the theoretical standpoint, as it represents a type of reaction catalyzed by acids to which less attention has been paid than those of ester hydrolysis and similar reactions. The present paper represents a brief study of the kinetics of the reaction in the presence of hydrochloric acid as a catalyst.

Experimental Methods

Materials.—Commercial creatine of very good quality was purified by two crystallizations from water, and was allowed to dry in the air. The product was pure white, odorless, and finely crystalline. Other reagents used were commercial c. p. products.

As analytical standards pure creatinine picrate² and creatinine zinc chloride were employed.

¹ Folin, Am. J. Physiol., 13, 48 (1905).

² Edgar, J. Biol. Chem., 56, 1 (1923).

Apparatus.—The reaction-velocity experiments were carried out in test-tubes fitted with rubber stoppers. These were kept at constant temperature by immersion in boiling water, alcohol or acetone, the mean temperatures being taken as 100°, 78° and 57°, respectively; a temperature of 25° was obtained by use of an electrically controlled thermostat.

For the analysis (colorimetric) a Duboscq type of colorimeter was employed, illuminated by a special colorimeter lamp.

Experimental Technique.—The pure creatine was dissolved in water and a measuredquantity of the solution was put into a test-tube and brought to the desired temperature. A definite quantity of standard hydrochloric acid (previously heated to the same temperature as the creatine) was then added, and the mixture placed in the constant temperature bath. A series of similar tubes was used in each run, in order to avoid loss of time in removing and measuring samples for analysis. At the end of given time intervals, separate tubes were removed from the bath and the reaction was stopped by adding immediately a quantity of sodium hydroxide solution equivalent to the acid, and cooling rapidly. The solution was then analyzed for creatinine formed, by the wellknown Folin¹ method, making use of the red color developed when creatinine is treated with picric acid and sodium hydroxide. A standard solution of creatinine (as picrate or as creatinine zinc chloride) was treated with picric acid and alkali in exactly the same way as the unknown solution, and the color was compared as usual. Repeated colorimeter readings were taken and all precautions necessary to obtain precise results with this method were observed. The accuracy is believed to be about 1% of the total creatinine present.

Results.—The results of a characteristic experiment are given in Table I, together with reaction-velocity constants calculated for a first order reaction. Table II gives the average values of the constants calculated from experiments under other conditions; the agreement of individual constants was in all cases similar to those in Table I. Table II also contains values calculated from an equation derived below.

Table I Results of Typical Experiment Temperature, 78° HCl, 0.76~M

Table II Average Velocity Constants

Expt.	Temp.	Conen. HCl Moles/liter	Initial conen. creatine Moles/liter	K found	K calc.
1	25	0.38	0.00750	0.0000340	0.0000314
2	57	.38	.0300	.000777	.000824
3	78	.19	.00447	.00256	.00254
4	100	.38	.0075	.02816	.0278
5	78	.38	.0075	.00494	.00512
6	100	.19	.00367	.01367	.0138
7	78	.76	.0300	.01235	.01245
8	78	.76	.0150	.01256	.01245

Discussion

General.—Reaction 1 proceeds in pure water to a condition of equilibrium³ in which the ratio of creatine to creatinine is of the order of unity. Creatinine is, however, much more basic than creatine, and in the presence of acid the reaction goes "to completion" with the formation of a salt of creatinine.⁴ It is obvious from the data in Table I, (confirmed by the actual data from which Table II is constructed) that under these conditions of experiment the reaction is essentially unimolecular. Whether or not an actual bimolecular reaction with the hydrogen-ion catalyst is involved⁵ cannot be determined from the data, although it seems probable from the data given in the following paragraph. It may be noted that combination of the creatinine with the acid presumably reduces the concentration of catalyst somewhat as the reaction proceeds; it is therefore necessary to keep the concentration of creatine small as compared with that of the acid; this has been done in all experiments, as is shown by the data in Table II.

The Effect of Acid Concentration.—The velocity constants obviously increase with the concentration of acid, increasing from the values in 0.19 N hydrochloric acid to those in 0.76 N acid (Expts. 3, 5 and 7, Table II), somewhat more rapidly than the increase of the acid concentration, although the slope of the velocity-constant—acid-concentration curve passes through an apparent minimum around 0.4 N hydrochloric acid. This is in accordance with data of other investigators on other reactions catalyzed by hydrochloric acid, and it seems probable that the velocity constants are proportional to the hydrogen-ion activity, although the data do not enable an exact comparison to be made.

The Temperature Coefficient.—The data in Table II show that at any given concentration of hydrochloric acid the effect of temperature may be expressed by the Arrhenius⁶ equation

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{E}{RT^2} \tag{2}$$

where E is the "critical increment" or "heat of activation." For a concentration of hydrochloric acid equal to 0.38 N the values calculated for the temperature intervals 25–57°; 57–78°; 78–100° are 19050, 20400, 20500 calories, respectively, indicating that for this temperature range E may be regarded as practically independent of the temperature. A similar calculation of the value of E for an acid concentration of 0.19 N and a temperature range of 78–100° gives a value of 19790 calories, indicating that for this range of concentrations E is independent of the acid con-

³ Myers and Fine, J. Biol. Chem., 21, 583 (1915).

⁴ Hahn and Barkan, Z. Biol., 72, 305 (1920), and many earlier references to various authors.

⁵ See Garrett and Lewis, This Journal, 45, 1901 (1923).

⁶ Arrhenius, Z. physik. Chem., 4 (1889).

centration. We can therefore express the velocity constants under the whole range of conditions approximately by the integrated equation

$$\ln K = -\frac{E}{RT} + C \tag{3}$$

where E has the mean value of 20,000 calories, and the value of the constant C depends upon the concentration of acid. Changing to ordinary logarithms, Equation 3 becomes

$$\log K = -\frac{4368}{T} + C' \tag{4}$$

the average values for the constants for the three acid concentrations being as follows: $0.19\ N$ HCl, C'=9.8496; $0.38\ N$ HCl, C'=10.1538; $0.76\ N$ HCl, C'=10.5400. If these values are substituted in Equation 4 and the values of K calculated for the different experiments we obtain the results given in the last column of Table II, which agree reasonably well with the experimental values. If the values of C are plotted against the acid concentration we may obtain by interpolation, values of the constant for any acid concentration within the range studied, which will enable the calculation of an approximate velocity constant at any temperature. This may be of use in determining the time necessary for practically complete conversion under various conditions, as in the analysis of creatine solutions.

It may be noted that the value for the critical increment is of the same order as that observed by various investigators for many other cases of acid catalysis in different types of reaction.

Summary

- 1. Measurements have been made of the rate of conversion of creatine into creatinine in hydrochloric acid solution at various temperatures and concentrations of acid.
- 2. The general nature of the reaction, and the influence of temperature and acid concentration are discussed.

UNIVERSITY, VIRGINIA

C'A

CA

[Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 151]

A STUDY OF THE MOVING BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS

By Duncan A. MacInnes and Edgar Reynolds Smith Received June 27, 1923

In our study of solutions of strong electrolytes it became desirable to obtain accurate transference numbers of a number of salts throughout a range of concentrations. From its apparent precision and the rapidity with which the measurements can be made, the moving boundary method

for obtaining these numbers seemed attractive, and a careful study of the method was accordingly undertaken.

As usually described, the moving boundary method for determining transference numbers is as follows. The transference number of one of the two ions of a salt is equal to the distance moved by the boundary of one of the ion constituents divided by the distances moved in the same time and under the same potential gradient by the boundaries of both ion constituents. These distances can be measured in an apparatus shown diagrammatically in Fig. 1. A solution of the salt CA under investigation is placed between one of CA' and another of C'A, having, respectively, the same cation and anion as the salt CA. The boundary at a and that at b are visible because of the different refractive indices of the solutions. On passing current through the apparatus the boundary a moves up to a' and the boundary b moves down to b'. The ratio: aa'/(aa' + bb') is equal to the transference number T_a . The solution of C'A must be lighter, and that of CA' heavier, than the solution of CA, and the ions C' and A' have smaller mobilities than the ions C and A, respectively, in order that the boundaries shall persist during the passage of current. The apparatus can also be constructed in the form of a U-tube, in which case both of the following or indicator solutions must be lighter than the solution whose transference number is being measured.

Fig. 1 Aside from the purely qualitative early work by Lodge¹ and others, the only workers who have published measurements made by this method are Denison and Steele,² and later Denison.³ These workers obtained a large amount of transference data including measurements on most of the more common strong electrolytes at various concentrations.

The authors of the present article have made an endeavor to extend and amplify Denison and Steele's work. In the first part of the investigation, after obtaining sharp and readily visible boundaries (which proved to be by no means easy), it was found that, although precise measurements could be obtained, the results were not reproducible unless all possible variables, such as impressed e.m.f. and the kind and the concentrations

¹ Lodge, Brit. Assoc. Repts., Birmingham, 1886, p. 389.

² Denison and Steele, (a) Phil. Trans., (A) 205, 449 (1906); (b) Z. physik. Chem., 57, 110 (1906-7).

³ Denison, Trans. Faraday Soc., 5, 165 (1909).

of the salts forming the indicator solutions, were kept constant. Also, the results obtained departed widely and erratically from the accepted values of the transference numbers. A single instance of the difficulties encountered will suffice. Measurements were made on a 0.1 N solution of potassium chloride, using 0.1 N lithium chloride and potassium acetate solutions as indicators. The "transference numbers" at 135, 230 and 325 volts were 0.638, 0.550 and 0.531, respectively. These values were reproducible to about 0.1% at each voltage, though they all depart widely from the correct value, 0.508.4 It is interesting to note that the values approach nearer to the correct number for the higher potentials. A change of the nature or concentrations of the indicator solutions leads to quite different results from those given.

From these and many other similar discouraging results it became quite evident that either the method was useless or some additional factor must enter. In correspondence with Professor Denison he suggested that the concentrations of the indicator solutions should be adjusted according to the relation,

$$C/T = C'/T' \tag{1}$$

in which C and T are the concentration and the transference numbers of the solution under observation and C' and T' are the corresponding values for the indicator solution. Kohlrausch, 4 in an early paper, derives this relation as a necessary condition for a stable moving boundary. He states, however, that the condition represented by that equation will automatically be established, if not present at the outset, from which it would be concluded that the initial concentration of the indicator solution is of little importance. Later, it was given a simpler derivation by Denison. 5 Denison and Steele^{2a} also state that the condition represented by Equation 1 establishes itself automatically, and give no limits to this spontaneous adjustment. These authors say, "It has been proved that the concentration of the lithium chloride (indicator solution) becomes automatically adjusted, so that the potential gradient is just sufficiently increased to make the lithium ions keep pace with the potassium ions," the latter being the ions of which the transference number is wanted. Denison⁵ has shown in his derivation that, under the conditions given, Equation 1 holds.

It became of interest to us therefore to determine (a) whether the boundaries move at the theoretical velocities if the condition given in Equation 1 is fulfilled at the boundaries, and (b) whether any of the automatic adjustment, predicted by Kohlrausch, takes place. It is evident that if the concentrations of the solutions must be exactly adjusted according to the ratio given by Equation 1, the moving boundary method is useless for obtaining transference numbers, since these numbers, as well as

⁴ Kohlrausch, Ann. Physik, 62, 209 (1897).

⁵ Denison, Z. physik. Chem., 44, 581 (1903). See also Miller, ibid., 69, 436 (1909).

those of the indicator solutions at a series of concentrations, must be known in advance. On the other hand, if there is even a small amount of the automatic adjustment predicted by Kohlrausch the correct transference numbers can be arrived at as the result of a series of experiments which approximate, more and more closely, to the theoretical conditions. This will be discussed more fully, later.

Because of a reduction of the number of variables and the ease of practical manipulation the apparatus we finally used involved only one moving boundary. If the current through the apparatus is kept constant throughout the experiment the transference number can be computed with as great accuracy as from the movement of two boundaries, provided, of course, that the boundary moves at the rate required by the theory under the conditions of the experiment.

The equations involved in the computation of the ionic mobilities and transference numbers when only one boundary is used are obtained as follows: If V is the velocity with which the ion constituent moves and U_1 its mobility, and ϵ the potential gradient then

$$V = U_1 \epsilon \tag{2}$$

Now the current through the tube, i, is determined by Equation 3, in which C is the concentration, A the area of tube and F the Faraday equivalent;

$$i = (U_1 + U_2) \epsilon CAF \times 10^{-3} = \epsilon \kappa A$$
 (3)

since the specific conductance, $\kappa = (U_1 + U_2)CF \times 10^{-3}$. From (2) and (3) then

$$U_1 = V \kappa A / i = l \kappa A / i t \tag{4}$$

in which l is the distance along the tube moved by the boundary in the time t.

From the mobility U_1 the transference number can, of course, be computed, but the transference number can also be computed from the measurements without a knowledge of the specific conductance, since

$$V = U\epsilon = T\Lambda\epsilon/F$$
now $\epsilon = i/\kappa A$ and $\Lambda = 1000\kappa/C$, therefore, ϵ

$$T = VCFA/1000i = lCFA/1000it$$
 (5)

Apparatus and Procedure

The cell shown in Fig. 2 was used for the study of the individual mobility of an ion constituent and the determination of transference numbers by the single boundary method.

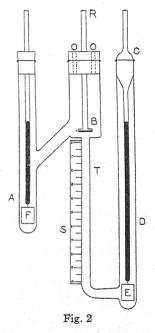
Let us consider the case of the measurement of the mobility of the potassium-ion constituent in a solution of potassium chloride. The electrode vessel D and measuring tube T are filled with the potassium chloride solution, which is kept out of

 $^{^6}$ Since lA is the volume swept through during the time t, and it is the number of coulombs, the transference number can be found by measurement with one boundary and a measurement with a coulometer in series, a principle we may make use of in future work.

B and A, and the combination ground glass stopper and electrode tube C is put firmly in place. In this case the electrode E is a piece of platinum gauze plated electrolytically with silver and then covered with silver chloride by electrolysis. This ground glass stopper C was used instead of rubber because the latter, when pushed strongly into the tube, may undergo a slow expansion which would influence the motion of the boundary. The glass rod R has a flat circular enlargement, B, on the lower end, which is tipped with a circular disk of thin rubber held on by a small central spot of de Khotinsky cement. This rod, which slides easily through the hole in the rubber stopper, is next pressed firmly over the top of T and the entrapping of air bubbles under it is avoided. Any excess of solution squeezed out of T and into B by this action is removed by a capillary pipet

thrust through one of the openings, marked O, in the rubber stopper. The electrode vessel A is then filled with lithium chloride solution and the anode F, which consists of a platinum gauze electroplated with silver, is inserted. The apparatus is next placed in a glass walled thermostat (regulated to $25^{\circ} \pm 0.05^{\circ}$), and the connections to the source of voltage are made. Then lithium chloride solution is pipetted through one of the openings marked O until B is filled. R is then gently loosened, but not yet pulled up, so that several milliamperes pass. The boundary between the lithium and potassium ions at once starts down the tube T. After the boundary has advanced about a centimeter the rod R is carefully pulled up. It was found possible to discard entirely the parchment paper used at the point corresponding to B in Denison and Steele's apparatus. The use of this paper is quite objectionable as it soaks up, from the tube T, solution which is afterward released into the indicator solution.

The boundary was rendered visible by means of an arrangement similar to that used by Denison and Steele. A sheet of white paper was fastened on a frame and placed behind the thermostat. Two electric light bulbs were put behind the paper. By means of a cord and pulley a piece of black cardboard could be raised and lowered between the illuminated paper and the back of the thermostat.



the thermostat. When the cardboard was raised to a position just below the boundary the latter became visible and could be read, on the scale S, readily to 0.1 millimeter.

The current through the tube, which was of the order of a few milliamperes, was maintained constant, within a few tenths of a per cent. by hand regulation of a rheostat in the circuit. Its value was known from the potential drop, measured with a potentiometer, across a standard resistance. The regulation was effected by observation of the scale of the galvanometer connected with the potentiometer. The source of current was a storage battery yielding 90 volts, to which was occasionally added a battery of dry cells. The volumes, corresponding to readings of the scale S in the tube T were obtained by means of a calibration with mercury. The length of T effective for measuring the motion of the boundary was 9 cm. and the scale S was graduated in millimeters. The position of the boundary could be estimated to the nearest 0.1 mm., so the precision of measuring the distance moved by the boundary was 0.2% or better.

The Experimental Results

All the figures obtained in a single experiment, with the apparatus just described, are given in Table. I These results show the constancy of the

velocity of the boundary during its whole passage down the tube, provided a constant current is sent through the apparatus. All the results given later in this article are averages of figures obtained as in this typical experiment and having about the same experimental accuracy. In making the readings times were read on the second that the boundary passed a given line on scale S.

TABLE I

Typical Experimental Results in the Determination of a Transference Number Solution, 0.1 N KCI; indicator solution, 0.065 LiCl; current, 0.005893 amp.; potential gradient, in KCl solution, 4 volts per cm.

Scale reading	0.50	5.50	5.80	6.10	6.40	6.70	7.00
Time, sec	0.0	1900	2016	2130	2243	2357	2472
Velocity, cm./sec., × 103		2.632	2.629	2.635	2.630	2.630	2.629
		,		I	lv. velo	eity	2.631×10^{-8}
				. A	Av, mob	ility	0.6578×10^{-1}

In all the experiments the cathode side of the apparatus was closed in order that there might be no movement of the boundary arising from changes of level of the solution due to the electrolysis. It is necessary, however, as G. N. Lewis⁷ has pointed out, to consider a correction for the volume change at the cathode during the passage of the current. However, at $0.1\ N$ this correction is only one part in 5,000 for both salts.⁸

It will be recalled that the main purpose of this investigation was to determine the effect of the concentration of the indicator solution, and the current density, on the velocities of the boundaries, and the resulting effect on the computed mobilities and transference numbers. In Tables II to V are given the results of measurements on boundaries formed, in each case, with the solution being measured at 0.1 N and varying concentrations of the indicator solutions. Tables II and III are the results obtained on the movement of the boundary between potassium and lithium chlorides with two different potential gradients in the tube, and Tables IV and V are corresponding results for potassium bromide solutions. The figures given in Tables IV and V are averages, in each case, of closely agreeing duplicates, whereas the corresponding figures in Tables II and III represent single experiments.

⁷ Lewis, This Journal, 32, 862 (1910).

⁸ Lewis' formula is: N=N'-vc, in which N is the Hittorf transference number, N' the uncorrected value from the moving boundary measurements, v the volume change at the electrode due to the passage of a Faraday, and c the concentration. The cathode reaction consists of (a) the formation of 1 equivalent of silver, (b) the formation of N equivalents of potassium halide and (c) the disappearance of an equivalent of AgCl. For KCl the resulting volume changes are (a) 10.3 cc., (b) 13.5 cc. and (c) 25.7 cc., the term (b) being the partial molar volume of KCl in 0.1 N solution, computed in the usual way from density measurements, multiplied by 0.49. The net change of volume is therefore 0.002 liter and the correction term 0.0002. The corresponding terms for KBr are (a) 10.5, (b) 17.3 and (c) 29.7.

TABLE II

Effect of Concentration of Indicator Solution on Movement of Boundary, Tenth Normal Potassium Chloride at 25°

Potential gradient in KCl solution, 4 volts per cm.

Conc. indicator soln. (LiCl)	Velocity Cm. per sec. × 103	$10^6 U_{ m K}$ in $0.1~N~{ m KCl}$	Transference number of K ion
0.1	2.713	(678)	(0.507)
.0887	2.663	(666)	(.498)
.08	2.654	(664)	(.496)
.075	2.641	(660)	(.494)
.07	2.633	658	.492
.065	2.631 .	658	.492
.06	2.637	659	.493
.055	2.658	(665)	(.497)
.045	2.622	(656)	(.490)
.035	2.615	(654)	(.489)

TABLE III

Effect of Concentration of Indicator Solution on Movement of Boundary, Tenth Normal Potassium Chloride at 25°

Potential gradient in KCl solution, 3.5 volts per cm.

Conc. indicator soln. (LiCl)	Velocity Cm. per sec. × 10 ³	$10^6~U_{ m K}$ in $0.1~N~{ m KCl}$	Transference number of K ion
0.1	2.373	(678)	(0.507)
.0887	2.324	(664)	(.497)
.08	2.312	(661)	(.494)
.075	2.309	(660)	(.493)
.07	2.303	657	. 492
.065	2.298	656	491
.06	2.296	656	.491
.055	2.309	(660)	(.493)
.035	2.287	(653)	(489)

TABLE IV

Effect of Concentration of Indicator Solution on Movement of Boundary, Tenth Normal Potassium Bromide at 25°

Potential gradient in KBr solution, 3.365 volts per cm.

Conc. indicator soln. (LiBr)	Velocity Cm. per sec. × 10°	$^{10^6}U_{ m K}$ in $0.1~N~{ m KBr}$	Transference number of K ion
0.1	2.557	(764)	(0.564)
.09	2.373	(709)	(.523)
.08	2.247	(671)	(.495)
.075	2.223	(664)	(.490)
.07	2.202	657	.485
.065	2.201	657	. 485
.06	2.272	(680)	(.501)
.05	2.275	(679)	(.501)

Fig. 3 is a typical diagram which represents the data given in the tables. The mobilities computed from the experiments are plotted as ordinates against the corresponding concentrations of indicator solution. A similar plot is obtained if the transference numbers are used instead of the mo-

bilities. The heavy line represents the values obtained at the higher potential gradient used and the lighter line those for a lower gradient. It will be seen from this plot, and also from the tables, that the velocity of the boundary (and therefore the computed mobilities and transference

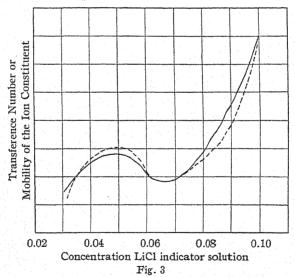
TABLE V

Effect of Concentration of Indicator Solution on Movement of Boundary, Tenth Normal Potassium Bromide at 25°

Potential	gradient	in	KBr	solution,	3.701	volts	per	cm.
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Conc. indicator soln. (LiBr)	Velocity Cm. per sec. \times 10 ³	$^{10^6U_{ m K}}$ in $^{0.1}$ N KBr	Transference number of K ion
0.08	2.465	(669)	(0.494)
.075	2.427	659	. 486
.07	2.423	658	. 486
.065	2.416	656	. 484
.06	2.498	(678)	(.501)
.05	2.497	(678)	(.501)

numbers) varies widely with the concentration of the following, or indicator, solution. However, at $0.065\ N$ for potassium chloride and at about the same concentration for potassium bromide there is a minimum in the curves. Within the experimental error the measured mobility at this



point is unaffected by changing the potential gradient. In addition, at this point, the relation between the concentrations of the measured and indicator solutions corresponds closely to Equation 1

$$C/T = C'/T'$$

For lithium chloride, for instance, the value for T' computed from Equation 1 is 0.320 whereas the results of MacInnes and Beattie⁹ give by inter-

⁹ MacInnes and Beattie, This Journal, 42, 1117 (1920).

polation the value of 0.316 for this concentration. The agreement would be exact if the minimum were taken as $0.064\,N$. In addition it will be seen, from an examination of the tabulated data, that on either side of the minimum there is a range of concentrations of indicator solution (about 5%) in which the measured mobilities and transference numbers are independent of this concentration within the experimental error. Apparently throughout this small range the automatic adjustment of the concentration of the indicator solution, as predicted by Kohlrausch, does take place. Outside this range the adjustment quite as evidently fails to occur. Erroneous values for transference numbers will therefore be obtained if the concentration of the indicator solutions is not adjusted within this range.

Some results have also been obtained which show that if the composition of the indicator solution is adjusted according to Equation 1, the transference number obtained by observation of the moving boundary is, within the experimental error, independent of the potential gradient. The figures are given in Table VI. The boundary becomes invisible, under the conditions of the experiments, with a potential gradient lower than about 2 volts per cm. If too large a potential gradient is used the boundary is distorted by heating effects.

Table VI Results of Moving Boundary Experiments at Different Potential Gradients Concentrations. KCl = $0.1\ N$; LiCl = $0.065\ N$

Current Amp. × 10 ³	Gradient (volts/cm.) in KCl solution	$10^6~U_{ m K}$	Transference number of potassium ion		
5.893	4	658	0.492		
5.156	3.5	657	.491		
4.420	3	656	.491		
4.051	2.75	660	.494		
3.683	2.5	657	.492		
3.315	2.25	657	.492		
2.951	2	No boundary visible			

In practical use of the moving boundary method for determining transference numbers an estimate of the probable value of the number should be made and the indicator solution concentration should then be computed according to Equation 1, and a measurement made. The indicator concentration should then be varied slightly and the measurement repeated. This should be continued until a portion of a plot similar to Fig. 3, and including the minimum value, can be prepared.

Further, the value obtained should be shown to be independent of the current through the apparatus, that is, to the potential gradients in the solutions. This procedure may sound tedious, but it is far more rapid, and also more accurate, than the determination of the same numbers by the Hittorf method. It also appears desirable that evidence showing that the adjustment of the compositions of the measured solution and the indicator

solution has been obtained, should be given in all future work with the moving boundary method.

It does not, at present, appear to be possible to give a clear picture as to why the boundaries move too fast on both sides of the "adjustment" represented by Equation 1, and why, on the side of a too dilute indicator solution, the apparent mobility passes through a maximum and then again decreases. Some experiments under consideration will, we hope, throw light on the subject. It seems probable, however, that if the adjustment to the conditions of Equation 1 cannot take place by the dilution of the indicator solution, the adjustment may occur in the leading solution.

The Transference Numbers

In this investigation we have obtained accurate transference numbers for potassium chloride and potassium bromide solutions at 0.1~N and at 25° . The value for potassium chloride, $0.492~\pm~0.001$, agrees substantially with the value, 0.493, given, by Denison and Steele. It is, however, somewhat lower than the number given by the Hittorf and e.m.f. methods, which average about 0.496.

Our transference number for potassium in potassium bromide, 0.485, lies between the value, 0.480, obtained by Denison and Steele by the moving boundary method, and the number, 0.495, found by Jahn and Bogdan¹⁰ at 18°, and the same value obtained at 25° by Pierce and Hart¹¹ in an extensive investigation by the electromotive-force method.

This investigation was originally undertaken to obtain data for a further test of the relation

$$T \wedge \eta^n = K \tag{6}$$

in which T is the transference number, Λ the equivalent conductance, η the relative viscosity, and the exponent n an empirical constant. For the series of alkali chlorides and hydrochloric acid K has been found, by one of the authors, 12 to be a constant at any one concentration. Physically, K is the conductance of the ion in a solution whose relative viscosity is unity. Table VII gives the data and the computation for the potassium ion from the two salts at $0.1\ N$ and 25° . The effect of the viscosity is small,

TABLE VII

CONDUCTANCE OF POTASSIUM ION AND THE INFLUENCE OF VISCOSITY

선생 등은 이 얼마나 되었다.	Λ	T_{K}	η	$T_{\mathbf{K}}\Lambda$	$T_{\mathbf{K}}\Lambda\eta$
KCI	128.99	0.492	0.9982	63.5	63.4
KBr	131.613	.485	.9946	63.8	63.5

¹⁰ Jahn and Bogdan, Z. physik. Chem., 37, 681 (1901).

¹¹ Pierce and Hart, This Journal, 43, 2483 (1921).

¹² MacInnes, ibid., 43, 1217 (1921).

¹³ Value determined by Stearn, *ibid.*, 44, 674 (1922), multiplied by 128.99/128.34, the ratio of Stearn's value of Λ for KCl to that recently determined by Kraus, *ibid.*, 44, 2422 (1922).

but noticeable, at this low concentration. The exponent, n, has been assumed provisionally to be unity. It appears then, for this limited amount of data at least, that within the limit of error Equation 6 holds for the potassium ion as well as for the chloride ion. It is hoped to extend this investigation to cover a wide range of strong electrolytes.

Summary

A modification of the moving boundary method of Denison and Steele for determining transference numbers, involving a single boundary, has been developed.

The boundaries move with the theoretical velocities only when the two solutions in contact at a boundary are adjusted, within about 5%, to the relation C/T = C'/T' in which C and C' are the concentrations and T and T' are the transference numbers. The correct value for T can therefore be obtained by a series of experiments approaching more and more closely to this condition. Unless this adjustment is obtained results are not independent of the composition of the indicator solution, or of the current through the apparatus, and may vary widely and erratically from the true values.

Transference numbers at 25° , for potassium chloride and potassium bromide in $0.1\,N$ solutions have been obtained. These numbers show that the conductance of the potassium ion is the same in these two solutions if correction is made for viscosity.

CAMBRIDGE 39. MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY, AND THE WESTERN ELECTRIC COMPANY, INC.]

THE WETTING OF GLASSES BY MERCURY¹

By Earle E. Schumacher Received June 30, 1923

A number of observers have held that mercury does not wet glass because the latter is always covered by a film of adsorbed gas which prevents the mercury from coming into real contact with the glass. If this view is correct then, as Bancroft² has pointed out, mercury should readily wet glass if the adsorbed gas were completely removed. In order to test the accuracy of this hypothesis, a number of experiments were performed in which mercury was placed in glass containers whose walls had been

¹ The term wetting is used in this paper in the sense that wetting is complete when the angle of contact between liquid and solid is zero and the meniscus concave, and that the liquid does not wet the solid in cases in which the angle of contact is zero and the meniscus is convex. In these experiments wetting was considered to have taken place whenever the meniscus of mercury was less convex at the conclusion of the experiment than it was at the start.

² Bancroft, J. Ind. Eng. Chem., 13, 88 (1921).

freed as far as possible of adsorbed gas. A description of several of these experiments will be given in this paper, together with a discussion of the results obtained and the conclusions reached.

Experimental Part

Fig. 1 illustrates the apparatus used in the first experiment.

The essential parts are the small aspirator, D, the distilling apparatus, B, the liquid air traps, G and F, and the mercury-vapor pump, H. In addition to the apparatus shown in this figure, two motor-driven oil pumps were utilized to maintain a suitably low pressure at the outlet of the mercury-vapor pump, H. All glass parts in the apparatus were made of soda-lime glass and before being used in these experiments, were cleaned with chromic acid and then thoroughly washed with distilled water. Immediately after the last washing the glass apparatus was sealed to the evacuating system and the water that still remained on the glass was pumped off.

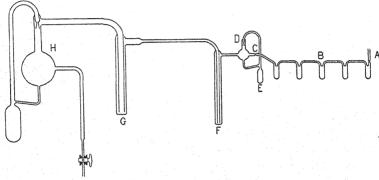


Fig. 1

At the start of the experiment the glass parts B, D and F, were subjected to a temperature of 400° for several hours, the pressure within the apparatus being maintained continuously at approximately 1×10^{-6} mm. of mercury, as measured by the Buckley type of ionization manometer. This treatment undoubtedly reduced the amount of adsorbed gas on these parts to a minimum. After this heat treatment the glass tube leading upward from Bulb A of the distilling train, B, was opened and redistilled mercury, purified according to the method recommended by G. A. Hulett,³ was introduced into Bulb A, after which the tube was immediately closed and the internal pressure again reduced to at least 1×10^{-6} mm. of mercury. The aspirator, D, was then kept at a temperature of 400° for approximately 50 hours and at the same time, 4 of the 5 bulbs in the distilling train were receiving similar treatment.⁴ By distil-

³ Hulett, Phys. Rev., 33, 307 (1911).

⁴ In this connection some consideration was given to the possibility of further reducing the amount of adsorbed gas on the glass by heating to higher temperature in a vacuum oven. On account of the physical limitation that would be imposed under this plan it seemed that the preliminary nature of the experiments did not warrant its adoption.

ling the mercury from one bulb to another it was possible to give the glass in the distilling train a good heat treatment, thereby freeing its surface of the adsorbed gas that was taken up when the mercury was introduced. Gases entrapped by the mercury were, of course, released and pumped out during this distillation of the mercury from one bulb to another. All glass parts in the distilling train received higher heat treatment during this heating than they ever received again during the experiment. After terminating the heat treatment to which the glass parts B and D were subjected, about 12 cc. of mercury was distilled over into D and the distilling train then sealed off at C. This amount of mercury was sufficient to cause the small aspirator, D, to function as such very satisfactorily. The distilling of the mercury in D, was continued for 50 hours and this was believed to have removed any gas that was still entrapped by the mercury.

The experiment described above was repeated five times, using different aspirators in each case, all of which, however, were made of soda-lime glass. In all of the experiments the conditions were maintained as near like those cited above as possible. In two of the aspirators, at the termination of the experiments, the mercury seemed to wet the glass slightly, while in the other three the mercury behaved just as it ordinarily does when placed in a glass container which has not been evacuated. In the two cases where a wetting seemed to occur, the surface of the mercury in Bulb E appeared to be perfectly flat. The mercury surface in one of these aspirators when exposed again to air slowly acquired a convex meniscus; the mercury in the other aspirator was not appreciably affected by air even after exposure for several days. In none of these experiments did the mercury ever assume a concave meniscus.

Additional experiments were conducted in a similar apparatus made of 702-EI Pyrex glass instead of soda-lime glass. The results obtained were about the same as those found when soda-lime glass was used, except that in the cases where there was evidence of wetting it usually took place more quickly. As it seemed possible that a correlation might exist between wetting and the chemical composition of the glass, further work was undertaken to investigate this point. For the small type of aspirator used in the above experiments an apparatus was substituted consisting of 6 bulbs sealed together. The first 4 bulbs, at the entrance of the train were made of soda-lime glass; the fifth bulb was made of Pyrex 702-EJ glass and the sixth bulb was of quartz. In several of these experiments a bulb made of Pyrex 702-P glass was substituted for one of the soda-lime bulbs. The soda-lime glass was sealed to the Pyrex bulb by connecting tubing made of glass varying in composition from that of the soda-lime glass at one end to Pyrex 702-EJ glass at the other. By means of a similar connecting tube, varying in this case from Pyrex at one end to quartz at the other, the Pyrex bulb was sealed to the quartz bulb. The bulbs, after being sealed to the evacuating system, were exhausted and with the pressure⁵ being maintained within them at approximately 1×10^{-6} mm. of mercury they were heated to a high temperature for about 50 hours, the soda-lime glass being kept at 400° while the Pyrex and quartz bulbs, by means of individual heating units, were kept at temperatures of 550° and 800°, respectively. After this heat treatment, which must have reduced the amount of adsorbed gas held by the glass to a minimum, mercury was distilled into the bulbs from a distilling apparatus such as was used in the experiment described above. After sufficient mercury had distilled into the bulbs to fill any one of them, the distilling apparatus was sealed off from the rest of the system. The mercury was then distilled from one bulb to another until the experiment was concluded; during this process whenever any bulb was empty it was always subjected to a heat treatment before mercury was again distilled into it. In each of these five experiments entirely new soda-lime and Pyrex bulbs were used. On account of the difficulty of obtaining satisfactory quartz bulbs, however, and also because of their high cost, it was necessary to use the same quartz bulb in all five cases.

In these experiments, the behavior of the mercury in the quartz bulb was extremely interesting. Before the curvature of the mercury showed any change in the soda-lime or Pyrex containers, it usually became quite flat in the quartz bulb. In only one experiment did the meniscus of the mercury actually become slightly concave, but in four other experiments the surface of the mercury was absolutely flat. In the previous experiments in which the small aspirators were used, if a wetting did occur there was always the possibility that something from the glass or some other source had contaminated the mercury, but here in the case of the wetting of quartz by mercury no such possibility existed. In every experiment during the early stages of the distillation the mercury that wet the quartz, when distilled again into the soda-lime or Pyrex glass bulbs, failed to show any wetting. The same mercury here wet in one bulb and failed to wet when distilled into another.

In these experiments with the bulbs, as in the experiments with the small aspirators, the behavior of the mercury in the Pyrex and soda-lime containers differed considerably from one experiment to another. In two of the experiments the surface of the mercury became quite flat in the Pyrex containers, but in at least four others it did not. In the two cases, the mercury was distilled from bulb to bulb for at least 30 hours before the flattening became at all pronounced. With the soda-lime glass bulbs, in only one case was there any noticeable change in the mercury surface,

⁸ It should be noted that pressures of this magnitude were maintained in all of these experiments. No degree of wetting was ever obtainable where higher pressures were maintained.

and that took place only after the distillation had continued for 50 hours. In this one case the mercury surface was still slightly convex after the experiment had been run for 75 hours. At the conclusion of this run the train of bulbs while still evacuated was sealed off from the rest of the system, the mercury was then poured from one bulb to another and measurements upon the curvature of the mercury surface in each bulb were taken. By properly mounting the bulbs the vibration of the mercury was reduced to a minimum and this made it possible to take fairly accurate readings. These measurements, which were taken with a cathetometer, are given in Table I and represent the differences in height between the places where the mercury cut the glass of the container and the top portions of the meniscus. For comparative purposes, measurements were also taken upon mercury in a soda-glass container that was evacuated but had never been heat-treated.

Table I Wetting Measurements

Type of glass:	Soda-lime unheated	Soda lime	702-P	702-EJ	Quartz
Diff. in height, mm.:	1.6	0.6	0.3	0.0	sl. concave

The chemical compositions of the various types of glass used are given in Table II. Glass 702-EJ was a borosilicate glass containing no metal of the magnesium-lime-zinc group nor any heavy metals, and the quartz was of course practically pure silica.

TABLE II

Chemical Compositions of the Glasses Used					
Soda lime	702-P	s	oda lime	702-P	
SiO_2	72.05	K_2O	0.10	1.12	
Al_2O_3	2.21	P_2O_5	0.08	Trace	
Fe ₂ O ₃ 0.19	0.05	Sb_2O_3	0.05	• • •	
PbO 1.44	6.11	MnO_2	0.09	0.01	
CaO 3.17	0.06	F_2	A	Trace	
MgO 0.03	0.09	B_2O_3	2.36°	14.07^a	
Na ₂ O	4.23				

[&]quot; By difference.

These results would indicate that a parallelism exists between wetting and the chemical composition of the glass. It is interesting to note that in a previous paper⁶ on "Measurements of the Gases Evolved from Glasses of Known Chemical Composition," a similar parallelism was found to exist between the amount of gas evolved by a glass and its chemical composition.

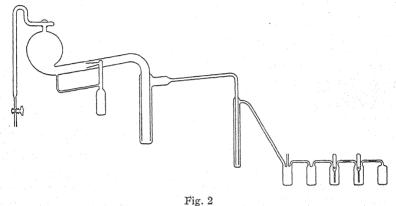
Fig. 2 shows diagrammatically the last type of apparatus worked with.

Here, as can be seen, capillary tubes were inserted in two of the bulbs; one made of soda-lime glass, the other of Pyrex. The small holes seen in the tubes just above the point where they become capillary, were to keep the pressure inside the capillary the same

⁶ Harris and Schumacher, Ind. Eng. Chem., 15, 174 (1923).

as in the outer bulb when the bottom of the capillary was closed by mercury. For denuding the glass of its adsorbed gas and for introducing the mercury into the apparatus, the methods employed in the preceding experiments were used.

Ten different runs were made with this type of apparatus. In one run a slight rise of the mercury in the capillary made of Pyrex glass was noted. In one other case there was neither a rise nor a depression in the Pyrex capillary. In 8 different runs the mercury was depressed in the Pyrex capillary. In no case was a rise observed in the soda-lime glass capillary.



Discussion

The results of the experiments that have just been described indicate that the chemical composition of the glass either directly or indirectly plays a part in determining whether or not mercury will wet the glass. The tendency of mercury to wet glass seems to decrease as the alkaline content of the glass increases. Similarly, as pointed out previously, the gas evolved from a glass increases as the alkaline content increases. A glass containing a high percentage of soda would be more easily hydrolyzed than one that contained a lower percentage, and the result of such an hydrolysis would be the formation on the surface of the glass of a thin film of sodium hydroxide, together with some amorphous silica. It is reasonable to assume, therefore, that mercury does not ordinarily wet a soda-glass surface because this film prevents it from ever touching the glass. On the other hand, such a film may have only an indirect effect on the wetting of glass by mercury due to the tenacious retention of large quantities of gas. If this alkaline film is either directly or indirectly responsible for the non-wetting of ordinary glass by mercury, then the results obtained in these experiments can be accounted for.

On the quartz surface, where there was no chance for an alkaline film to exist, a degree of wetting was always obtained. On the surface of Pyrex glass the alkaline film would surely be thinner than on the soda lime glass

and, as will be recalled, mercury seemed to show a greater tendency to wet Pyrex than it did soda-lime glass. That on two occasions a degree of wetting was noted when a soda glass was used can be accounted for by assuming that the specific conditions of washing and subsequent drying of the soda glass were such as to prevent any appreciable alkaline film formation. In the case of the capillary tubes, on the other hand, no marked wetting ever occurred in the capillaries because a longer period of time was required to remove the water from within these tubes than from surfaces outside, and this was favorable to the formation of alkaline films.

Summary

An attempt has been made to cause mercury to wet glass and quartz after their surfaces have been denuded of gas as far as it is possible with the present means at our command. The difficulty of this task appears to become greater as the alkaline content of the glass increases. Fairly good wetting can generally be obtained on quartz, while on Pyrex and sodalime glass it is obtained only occasionally.

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[Contribution from the Department of Chemistry of West Virginia University]

LIESEGANG RINGS. III. THE EFFECT OF LIGHT AND HYDROGEN-ION CONCENTRATION ON THE FORMATION OF COLLOIDAL GOLD IN SILICIC ACID GEL. RHYTHMIC BANDS OF PURPLE OF CASSIUS

By Earl C. H. Davies RECEIVED JULY 2, 1923

Introduction.—In a previous paper¹ the author showed that light has a pronounced influence on the tendency for colored bands of colloidal gold to form in silicic acid gel. It was the purpose of the present work to make a more exhaustive study of this light effect. The following factors were investigated: the effect of light of different wave lengths; the relation between band formation and hydrogen-ion concentration; the variation of band formation with kind of acid used in making the silicic acid gel; the effect of variation of oxalic acid concentration; the result of using different strengths of gold chloride solution; the result of replacing the oxalic acid by other reducing agents.

The Effect of Light of Different Wave Lengths.—For the first series of experiments, glass cylinders, 18 × 5 cm., were fitted with large corks holding 2.5cm. test-tubes, within which were smaller tubes, containing the gel in which diffusion was to take place. Some of the gel was protected by

¹ Davies, This Journal, 44, 2700 (1922).

black glazed paper. Other tubes were protected by grids made by cutting horizontal, parallel slits 2mm, wide out of the black paper. These slits were 8 mm. apart. Other tubes were unprotected from the light rays, except by a total thickness of 5.1 mm. of nearly colorless glass, and the respective liquid, which was between the large test-tube and the wall of the cylinder. Tests were made in duplicate. Since the intensity of light varies inversely with the square of the distance, some samples were placed in the circumference of a circle of 30cm. radius at the center of which were 2 Edison Lamps "100 Watts, 115 Volts. P. S., 25 Mazda C." Other similar samples were put in the circumference of an outer concentric circle of 43.5cm. radius. Hence, the light intensity in the outer circle was to that in the inner circle as $(30)^2/(43.5)^2$ or about 1/2. The cylinders in the inner circle were spaced in such a way that they did not shut off the light from the farther cylinders. Solutions were so chosen that the light transmitted was of the different wave lengths present in the visible spectrum. The outer cylinders contained, respectively, air, water, 1 M cobalt nitrate, 0.001 M potassium permanganate, 0.01 M potassium permanganate, 1 M copper sulfate, 1 M nickel nitrate, and 1 M potassium dichromate solutions.

The silicic acid gel was made by slowly adding 500 cc. of water glass (d., 1.16) to a mixture of 500 cc. of 2.975 N sulfuric acid and 40 cc. of 1% gold chloride solution. The mixture was filtered before use. The water glass was of such composition that, with congo red as indicator, it was 1.564 N at d., 1.16 and 0.585 N at d., 1.06. Three days were allowed for the gel to set in the test-tubes. Five cc. of saturated oxalic acid solution was then added to each tube.

The experiment was run for 3 weeks without disturbing the lights or tubes. At the end of this time in no case did I find any evidence of bands in the gel samples which had been protected by black paper. Neither were there bands in the tubes protected only by the potassium dichromate solution. In all other cases of tubes exposed continuously to light some gold was reduced to the colloidal condition. The tubes with only air and glass as absorbent had at the top a purple region 7mm, wide, fading to a light green. There were faint, light green, double bands at 4.6, 5.6, 6.4, 7.7, 8.3 and 9.5 cm., respectively, from the top. These bands slanted toward the light and tended to be double, due to the fact that two bulbs were used instead of a point source of light. They were caused by irregularity of light intensity. The tubes with the grids showed, at each opening, reduction similar to the comparable position in an open tube. Behind the dark portions of the grids the results were very similar to the dark tubes at comparable depths but there appeared some effect of light due to reflection. Tubes more distant from the light showed less color than those in the inner circle. The order of decreasing reduction, that is, of decreasing tendency to form colloidal gold, was found to be: air, inner circle; air, outer circle; water, inner; water, outer; 1 M cobalt nitrate; $0.001\ M$ potassium permanganate; $0.01\ M$ potassium permanganate; $1\ M$ copper sulfate; $1\ M$ nickel nitrate; $1\ M$ potassium dichromate; and no light. However, $1\ M$ potassium dichromate and black paper protected the gold equally well.

This series of experiments shows conclusively that light of short wave length is responsible for catalyzing the formation of colloidal gold in silicic acid gel, when the experiment is carried out according to the directions of H. N. Holmes.² When the diffusion takes place in the dark only the larger particles of yellow gold crystals are produced. The beautiful, multicolored zones obtained by Holmes were not true Liesegang bands, for the latter would be formed in the dark and their distance apart would increase going from the top to the bottom of the gel. I have obtained these same colored zones but only in changing light, when Holmes' directions were followed. In connection with these bands, in his book on colloidal chemistry, Bancroft⁸ says, "He (Holmes) has put forward a theory of rhythmic banding which unfortunately does not account for the fact, recorded in the same paper, that colloidal gold gives three bands, red, purple and blue, before repeating." My present work plainly removes the only objection that Bancroft has offered to the theory advanced by Holmes. Whether Holmes' theory is general in its application is, of course, another matter.

Lecture or Laboratory Demonstration of the Effect of Light on Reduction of Gold.— To 25 cc. of 3 N hydrochloric acid add 2 cc. of a 1% solution of gold chloride. Shake this mixture while adding slowly 25 cc. of water glass (d., 1.16). Filter the liquid into 2 test-tubes and allow the gel to set for 3 days. Cover with black paper. Add to each tube 5 cc. of a saturated solution of oxalic acid. Place in a dark room and allow to diffuse for 3 weeks. Open a tube in bright sunlight and with a stopwatch record the time when color appears. When a tube is first opened only a few crystals of gold will be seen, but soon the color of colloidal gold will appear.

With such a tube I obtained a color flash in the upper part in 50 seconds. The time varies with light intensity. Hence the experiment may be used to measure the latter. The great rapidity, with which the color deepened, was very striking. After 3 minutes colloidal gold extended from a position 1.5 cm. from the top to the bottom of the tube. In the zone from 1.5 to 1.8 cm. it was a beautiful red; in the zone from 9.6–12 cm. the color shaded to purple. When 3 N sulfuric acid is used instead of the hydrochloric acid, the diffusion should not be allowed to continue for so long a time. Striking results may be obtained from the gel made with 3 N sulfuric acid by exposing it to light for a few minutes on the third day, and then each week until diffusion has reached the bottom of the tube. In this way the colored zones will be separated by nearly colorless ones.

Relation between Band Formation and Hydrogen-Ion Concentration.— This relation was studied in two ways, one direct, and the other more indirect. I used 76 tubes of gel for this phase of the work. Results, in Table I, are confined to shielded and open tubes. To make the gel, 6 cc. of 1% gold chloride solution were added to 75 cc. of the acid. To this

² Holmes, This Journal, 40, 1190 (1918).

³ Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1st ed., p. 259,

mixture were then added 75 cc. of filtered water-glass solution, and the product was quickly poured into test-tubes. After 3 days, gels with 0.67 N acidity were satisfactory. With the gels of lower hydrogen-ion concentrations setting occurred in less than 2 minutes.

TABLE I

RELATION BETWEEN HYDROGEN ION AND COLOR OF COLLOIDAL GOLD ⁴							
Acid	Acidity of mixture N	After standing in the dark 4 days	28 Cm. from lights	Exposed to sunlight after 3 days in dark			
HNO_3	0.67	Very light blue	Some blue to	In 50 sec. blue zone started at			
		to 2 cm.	2.1 cm.	4.3 cm. and reached 5.7 cm. in less than 5 min.			
HNO_3	0.045	Slight purple to 7.5 cm.	Purple to 8 cm.	In 1 min. 5 sec. a blue zone appeared between 6.4 and 7.4 cm.			
HNO_3	0.012^a	Very light purple	Green to violet	In 1 min. 40 sec. a light blue zone appeared at 5.7 cm.			
HC1	0.664	A few yellow crystals	Green, brown, yellow	In 43 sec. purple began at 0.7 cm. Final colors, blue, red, blue. Very pretty.			
HCI	0.034	Slight purple to 7.3 cm.	Purple to 8 cm.	Not observed in sunlight on third day.			
HCI	0.012^{a}	Slight purple to 6 cm.	Violet light, brown	In 28 sec. a purple zone came at 3.7-4.9 cm. In 3 min. 45 sec. light purple at 6.2-7.7 cm.			
H_2SO_4	0.67	Gold crystals	Light blue, green, yellow	In 7 min. 30 sec. with carbon are light, old rose red at 3.7–4.7 cm.			
H_2SO_4	0.012^{a}	Violet to 6.7 cm.	Blue, violet, brown	In 40 sec. a purple blue zone appeared at 5.6–6.8 cm.			
H ₂ SO ₄	0.021^{a}	Slight purple to 6.7 cm.	Purple to 8 cm.	In 2 min. 28 sec. a distinct blue zone appeared at 6.6–7.2 cm.			
HC₂H₃O	2 0.67	Slight blue to 2.2 cm.	Slight green, blue to 2.1 cm.	In 28 sec. a purple zone began at 4 cm. After 3 min. 45 sec. it had extended to 4.7 cm.			
HC ₂ H ₃ O	0.047	Violet to 7.3 cm.	Purple to 8 cm.	No change in 10 minutes.			
HC ₂ H ₃ O	0.012^a	Wine color to 6.2 cm.	Wine color Very pretty	No change in 10 minutes. Very pretty.			

a Basic.

Conclusion in Regard to Hydrogen-effect in the Dark.—With the acids used, and at the concentration of these experiments, the decreasing order of hydrogen-ion concentration is nitric, hydrochloric, sulfuric, and acetic acids. The nitric and hydrochloric acids furnish nearly the same hydrogen-ion concentration. In keeping with this, I found that, with the final concentration of 0.67 N nitric and hydrochloric, scarcely any reduction took place in the dark. With sulfuric acid the reduction was to yellow

⁴ Red gold indicates small particles and hence also small "pockets." Blue gold indicates larger particles, and green still larger ones. A saturated solution of oxalic acid was used above the gel as the reducing agent.

crystals, and no colloid was formed in the dark. With acetic acid, in the dark, the reduction took place sufficiently rapidly to give the purple colloid. Similarly, when we consider the decreasing hydrogen-ion concentrations for each of the several acids, we find that there is a regular tendency for the reduction in the dark to take place more rapidly in the more basic gels. Take, for example, the concentrations of acetic acid recorded in Table I. With a final normality of 0.67, a slight blue developed to 2.2 cm. from the top. With a final acid normality of 0.047 the violet color extended to 7.3 cm. With the 0.012 N basic gel a wine color developed. So, also, in the other cases in the dark the most rapid reduction and hence the smallest colloidal particles occur where hydrogen-ion concentration is lowest.

In the Light.—When diffusion takes place in continuous, uniform light, we have the same relation between hydrogen-ion concentration and rapidity of reduction as we have in the dark. The difference is that in all cases the light hastens reduction, but it does not disturb the regularity of the hydrogen-ion relation. For example, in the case of acetic acid at $0.67\,N$ a slight green-blue was developed, showing that relatively large particles were present and hence reduction had occurred in large "pockets." With $0.047\,N$ acidity the color is purple. With $0.012\,N$ basic the color is like that of wine.

Hence, it appears from this series of experiments that where the hydrogen-ion concentration is relatively low we have reduction in small "pockets." I have spoken of this as "rapid" reduction. The effect of the light is comparable to a rapid decrease of hydrogen-ion concentration.

Besides the experiments recorded, I performed a series in which the final normality of the sulfuric acid in the gel was 2.1. With such a large hydrogen-ion concentration there was slightly more reduction to colloidal gold than with the $0.67\ N$ sulfuric acid; but, when exposed to the light, gels made with this acid gave very little further reduction, whereas a check tube of $0.67\ N$ excess acid gave reduction in the light in 42 seconds. Hence, we are driven to the conclusion that the influence of light shows up best at a final hydrogen-ion concentration of less than $2.1\ N$ and approximately $0.67\ N$.

The Variation of Band Formation with the Kind of Acid Used.—Hydrochloric acid and nitric acid give gels which behave quite similarly, but that from hydrochloric acid is better where the light effect on the gel is to be studied. In comparing similar hydrogen-ion concentrations it seems that the gel made with sulfuric acid shows a greater tendency for the reduction of gold than does that made with hydrochloric acid. Such differences are due to the presence of different salts which have an influence on the rate of peptization and hydration and hence help to govern

Table II

Reduction of Gold in Silicic Acid Gel with Reducing Agents Other than Oxalic

Acid

Acid	Substance in gel ^a	Substance above gel	Results in continuous ^b light, 4 days	Results in dark	At 42 cm. from Balopticon lens
H ₂ SO ₄	1% AuCla		Green, yellow, over 25 plates	Cryst. Au, 30 plates	In 10 sec. light red color at 1.0-5.6 cm.
HCI	1% AuCls	10% phenyl-	No colloidal Au, or band	Cryst. Au, 10 plates	In 9 sec. light red color at 0.0-5.7 cm.
H ₂ SO ₄	10% AuCla	hydrazine, in alcohol	Brown, black, 50+ plates	Brown, black, 50+ plates	In a few sec, very light red at 3.8-4.8 cm.
HCI	10% AuCis		Colorless, 50+ plates	Colorless, 50+ plates	In 2 min. 10 sec. red, black
H ₂ SO ₄	0.25% phenyl- hydrazine, in alcohol	10% AuCls, mottled	Dark brown, mottled many plates	Brown, mottled many plates	No change in 15 min.
HCI	0.25% phenyl- hydrazine in alcohol	10% AuCla	Green, brown, many plates	Green, yellow	More black in 10 sec.
H ₂ SO ₄	1% AuCla	40% HCHO	Similar to orig.	Very few Au	Very slight red before 5 min.
HCI	1% AuCls	40% HCHO	Similar to orig.	No change	No change in 6 min.
H ₂ SO ₄	10% AuCla	40% HCHO	Few Au cryst.	Few Au cryst.	No change in 6 min.
HCI	10% AuCls	40% HCHO	No change	No change	No change in 6 min.
H ₂ SO ₄	0.25% for- maldehyde	10% AuCla	Yellow, no re- duction	Yellow, very slight pink	In 25 sec. pink became more intense
HCI	0.25% for- maldehyde	10% AuCle	Yellow, no re- duction	Yellow, no re- duction	No change in 13 min.
H ₂ SO ₄	0.1% glucose	10% AuCla	Lightred, brown, regu- lar bauds ^d	Lightred, brown, regu- lar bands ^d	Little change in 12 min.
HCI	0.1% glucose	10% AuCla	Yellow, no re- duction	Yellow, no re- duction	No change in 9 min.
H ₂ SO ₄	0.1%AuClaa)		Blue, purple	Blue, purple	Little change in 11 min
HCI	0.1% AuCia		Liesegang bands, "pur-	Liesegang bands, "pur-	No change in 10 min.
		10% SnCl ₂ , + 0.1% SnCl ₄	ple of Cas- sius"	ple of Cas- sius"	
H ₂ SO ₄	10% AuCla		Brown, yellow	Brown	In 55 sec. top of brown turned black
HCI	10% AuCla		Brown, to deep purple bands	Brown, to deep purple bands	No change in 6 min.
H ₂ SO ₄	0.25% SnCl ₂ - SnCl ₄ mixt.	10% AuCla	Light to dark brown	Light to dark brown	No change in 8 min.
HC1	0.25% SnCl2-	10% AuCla	Top 2 cm. clear	Top 2 cm. clear	No change in 5 min.
	SnCl ₄ mixt.		yellow, lower	yellow, lower	
			portion	portion	
			brown, with bands	brown, with bands ^f	

^a 1 cc. for every 25 cc. of mixture, except with glucose where 0.1% means the percentage of solid glucose in the gel.

^b Later observations, after 3 weeks, on the duplicate tubes, showed that the results at 4 days were typical of the longer period.

^e These were present in all tubes in which phenylhydrazine was used. They were cleavage planes, of varying sizes up to 4.2 by 1.5 cm.

d These bands were light, reddish-brown, about 1 mm. wide. They were, starting

the size of the "pockets." However, the kind of acid is of far less importance than the concentration of hydrogen-ion present.

The Effect of Variation of the Concentration of Oxalic Acid.—My experiments show that in the case of the gel made with sulfuric acid the strength of oxalic acid solution may vary between saturated and 1/4 saturated, and perhaps may be even less, without effecting any great change in results. However, it is to be recommended that a saturated solution of oxalic acid be used.

The Results Obtained with Different Strengths of Gold Chloride Solution.—In Table II results are recorded of the effects of different reducing agents diffusing into gels, containing 1 cc. of 1 to 10% gold chloride in each 26 cc. There seems to be no advantage in having the gel contain more than 0.04% by weight, of gold chloride, while 0.4% gold chloride seems too concentrated for use.

The Effects of Replacing the Oxalic Acid by other Reducing Agents.— 136 Tubes of gel were made up in many different ways. The conditions governing the use of continuous light, grids, and control of the operations in the dark were observed also in these cases. The sulfuric acid used was 2.975 N and the hydrochloric acid was 2.967 N. The water glass was d. 1.16 and was 1.584 N. To 75 cc. of the acid was added 6 cc. of the gold chloride solution or the reducing agent (in the cases where the gold chloride was placed above the reducer); 75 cc. of filtered water glass (d., 1.16) was then added and the mixture constantly and vigorously shaken, and poured into 15mm. test-tubes to set. Three days were allowed for setting; after which some of the tubes were covered with grids or dark paper and all were put in the dark room at the same distance from the light, as described earlier in this paper. Illumination was continuous for three weeks.

Conclusion in Regard to Reducing Agents other than Oxalic Acid.—The most interesting set of experiments was with the formation of purple of Cassius. Formaldehyde and phenylhydrazine in alcohol are not suitable for this type of experiment. The results obtained when a 10% gold chloride solution diffused into a silica gel made with sulfuric acid and containing 0.1% glucose were remarkable in that regular bands were obtained but they were equally spaced, whereas the true Liesegang rings are at the top, at 3.7, 4.1, 4.45, 4.8, 5.1, 5.4, 5.7, 6.0, 6.25, 6.5, 6.8, 7.3, 7.7, 8.0 and 8.3 cm., respectively.

^e In the upper part of the tube the color was so intense that the bands were indistinct. In the lower part the purple bands were sharp. At 8 cm. they were 2.5 mm. apart, and they were true Liesegang bands.

f This was peculiar in that the concentrated AuCl₂ solution seemed to have dissolved the brown precipitate in the upper 2 cm. region. The bands in the brown portion were true Liesegang bands, but were difficult to see on account of the nature of the precipitate. At 4 cm. from the top, they were 1.5 mm., and at 9.7 cm. they were 5 mm. apart.

developed farther and farther apart. I shall refer to this striking phenomenon in a later paper.

Rhythmic Bands of Purple of Cassius.—Narrow but distinct rhythmic bands of purple of Cassius are obtained as follows. To 12.5 cc. of $3\ N$ hydrochloric acid add 1 cc. of 1% gold chloride solution. Shake the mixture vigorously while adding 12.5 cc. of water glass (d., 1.16). Allow the liquid to set in a test-tube for 3 days. Add 3 cc. of a mixture made from the equivalent of 10 g. of anhydrous stannous chloride and 0.1 g. of anhydrous stannic chloride in 90 g. of water. This mixture is turbid and, therefore, must be shaken vigorously before it is used. During the diffusion, the turbidity entirely disappears. When heavier bands are desired they may be obtained by using more concentrated solutions of gold chloride up to 10%; but when these more concentrated solutions are used the zones between the bands are not so free from residue.

Summary

- 1. Experiments have been performed which show that gels made with silicic acid and gold chloride are remarkably affected by light and that it is the light of short wave length which functions thus.
- 2. The results obtained remove Bancroft's objection to Holmes' diffusion theory of Liesegang band formation.
- 3. Another series of experiments has shown that there is a distinct relation between hydrogen-ion concentration and the size of "pockets" in which the gold is formed.
- 4. Directions are given for a striking lecture or laboratory experiment to show the influence of light on reduction.
 - 5. Purple of Cassius was obtained in true Liesegang bands.

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[CONTRIBUTION FROM THE EPPLEY LABORATORY]

THE TEMPERATURE COEFFICIENTS OF UNSATURATED WESTON CELLS

By Warren C. Vosburgh and Marion Eppley Received July 3, 1923

The unsaturated Weston cell, although not a true standard cell, is widely used as a secondary standard of electromotive force because of its low temperature coefficient. Jaeger¹ stated that the electromotive force of a cell of this type with a cadmium sulfate solution saturated at 4° as the electrolyte could be regarded as practically constant at all ordinary temperatures. Dearlove² found a temperature coefficient —0.00003 volts

¹ Jaeger, "Die Normalelemente," Wilhelm Knapp, Halle a.S., 1902, p. 86.

 $^{^2}$ Dearlove, *Electrician*, 31, 645 (1893). Dearlove does not state the concentration of cadmium sulfate in the electrolyte of his cells but the electromotive forces indicate that it was smaller than that of a solution saturated at 4° .

to —0.00007 volts per degree. The present investigation was undertaken to supply more definite information as to the magnitude of the temperature coefficient of unsaturated Weston cells.

Materials

Cadmium Sulfate.—A good grade of commercial cadmium sulfate was thrice recrystallized slowly at room temperature, or slightly above, the third time from redistilled water slightly acidified with sulfuric acid.

Mercurous Sulfate.—The mercurous sulfate designated as No. 1 was prepared electrolytically from mercury which had been purified by electrolysis. The apparatus was similar to that of Hulett, and the current density was 0.5 amp. per sq. dm. The amount of finely divided mercury in the mercurous sulfate was found to be dependent on the rate of stirring, a whiter product being obtained with more vigorous stirring. The

mercurous sulfate was allowed to stand for several months under 0.02 M sulfuric acid solution. It was then digested for 5 days at a temperature near the boiling point with 1.8 M sulfuric acid and kept under the acid solution in the dark until used.

Mercurous sulfate No. 2 was prepared by reducing mercuric sulfate with formaldehyde.⁴ Mercuric oxide of c. P. quality was added to a large excess of hot 4 M sulfuric acid solution, an excess of formaldehyde added and the solution maintained at 100° until precipitation was complete. The precipitate was washed and maintained at boiling temperature for several hours under 1.8 M sulfuric acid solution and kept under a 1.8 M acid solution in the dark.

Mercurous sulfate No. 3 was obtained by allowing a portion of the mercuric sulfate solution used in the preparation of No. 2 to stand at room temperature after addition of formaldehyde. It was washed and kept under $1.8\ M$ sulfuric acid solution in the dark.

Mercury.—Commercial redistilled mercury was purified by electrolysis as described by Wolff and Waters⁵ and twice redistilled by Hulett's method.⁶

Cadmium Amalgam.—Cadmium was deposited electrolytically from a concentrated solution of the purified cadmium sulfate, the cathode consisting of a weighed portion of the mercury described above. When sufficient cadmium had been deposited the amalgam was weighed, mercury added to bring the cadmium concentration to 12.5%, and the amalgam melted by gentle heating and well mixed.

Vessels.—Glass H-vessels of the type shown in Fig. 1 were used.

Apparatus

Potentiometer.—The potentiometer described by Eppley and Gray⁷ was used, the working battery consisting of 2 large capacity cadmium cells. Cell comparisons with this instrument were reproducible to 1 or 2 microvolts. For measuring Cells 56–60 and the normal cells at 45° a commercial potentiometer was used. It was calibrated over the range of the other potentiometer by making cell comparisons by means of both instruments. The correction at the upper limit of this range was assumed to apply to

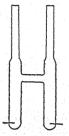


Fig. 1.— Type of Hvessel used. The length was about 13 cm. and the inside diameter of the lower parts of the legs 1 cm.

⁸ Hulett, Phys. Rev., 32, 262 (1911).

⁴ Deniges, Ann. chim. phys., [7] 18, 397 (1899).

⁵ Wolff and Waters, Bur. Standards Bull., 4, 10 (1907).

⁶ Hulett, Phys. Rev., 33, 307 (1911).

⁷ Eppley and Gray, J. Optical Soc. Am., 6, 859 (1922).

the readings of Cells 56-60, and that at the lower limit to to the readings of the normal cells. The corrected readings thus obtained must have been accurate to 0.00004 volt. The temperature coefficients should be more accurate than this, however, as readings could be duplicated to 0.00001 volt, and some errors must have been cancelled by the subtraction.

Both potentiometer systems were shielded as recommended by White.8

Standards.—Three well-aged, very constant, normal cells made at the National Physical Laboratory at Teddington, England, and furnished to this Laboratory through the kindness of Dr. F. E. Smith, were used as the reference standards. Their values were assumed to be such that the normal cells made in this investigation would have a value of 1.018054 volts at 25°.

Temperature Control.—Two oil thermostats, maintained constant within 0.02°, were used for regulation of the temperature. One was kept at 25° and contained the reference and working standards; the other contained the experimental cells, and its temperature was changed as desired. Temperatures were determined by means of a thermometer recently calibrated by the Bureau of Standards, and were accurate to 0.03°.

Preparation of the Cells

The platinum wires in the mercury legs of the vessels were amalgamated and the amalgam and mercury introduced as described by Wolff and Waters. A 0.015 M sulfuric acid solution, prepared from water redistilled from alkaline permanganate, was saturated with cadmium sulfate. Fifteen normal cells were prepared using this solution, 10 but otherwise as described by Wolff and Waters.9 Cells 1 to 5 were prepared with mercurous sulfate No. 1, Cells 6 to 10 with No. 2, and Cells 11 to 15 with No. 3. For the unsaturated cells, portions of the saturated solut on were diluted with from 2.5 cc. to 50 cc. of the 0.015 M acid solution to a liter, as shown in Table I. The mercurous sulfate, No. 1, was washed well with the cadmium sulfate solution to be used in the cells and introduced into the vessels by means of a pipet. Cadmium sulfate solution was then run in until the level was above the cross-arm. The air was displaced by nitrogen which had been washed with water and concentrated cadmium sulfate solution, and the upper ends of the glass tubes hermetically sealed. Special precautions were taken to prevent evapora-

- * White, This Journal, 36, 2011 (1914).
- 9 Ref. 5, p. 30.

10 Hulett [(a) Trans. Am. Electrochem. Soc., 14, 89 (1908)] found that Weston cells with acid electrolytes were remarkably constant in electromotive force, and Smith [(b) Electrician, 75, 463 (1915)] and Obata [(c) Proc. Math. Phys. Soc. Japan, 2, 232 (1920)] found that Weston normal cells were more constant if the electrolytes were acid than if they were neutral. Obata determined the relation of the electromotive force to the acid concentration, and on the basis of his results it was calculated that an electrolyte containing 0.0115 moles of sulfuric acid in a liter (resulting from the saturation of 0.015 M sulfuric acid with hydrated cadmium sulfate) would give cells with an electromotive force 20 microvolts lower than that of the neutral cell. Obata's acid cells were all more acid than this, but some experiments in this Laboratory have shown that his relationship holds for low acidities also, contrary to the statement of Hulett (Ref. 9a, p. 80).

tion of the electrolyte. The cells were mounted on racks, copper connecting wires being soldered to the platinum wires and to short copper rods¹¹ inbedded in a hard rubber plate.

The concentration of cadmium sulfate in the various solutions was determined by evaporating 3 to 5 g. samples to dryness, with the addition of a little sulfuric acid. The residue was brought to constant weight by adding 1 or 2 drops of concd. sulfuric acid, heating with a medium flame, cooling, adding more acid, and heating with a low flame until the acid was completely expelled.¹² Three determinations were made on each solution, and the average results together with the average variations are given in Table I.

Table I

Composition of Cadmium Sulfate Solutions and Electromotive Forces of Cells

Solution no.	Cells	Dil. acid added Cc.	CdSO4	E.m.f. at 25° Average volts
1	16-20	None	43.22 ± 0.01	1.018270 ± 0.000008
2	41-45	2.5	$43.12 \pm .03$	$1.018374 \pm .000007$
3	21-25	5	$43.06 \pm .00$	$1.018548 \pm .000005$
4	26-30	9. 1	$42.94 \pm .01$	$1.018711 \pm .000013$
5	31-35	11	$42.90 \pm .01$	$1.018788 \pm .000007$
6	36-40	15	$42.77 \pm .04$	$1.018983 \pm .000006$
7	46-50	22.5	$42.63 \pm .00$	$1.019343 \pm .000007$
8	51-55	30	$42.39 \pm .01$	$1.019688 \pm .000014$
9	56-60	50	$41.84 \pm .02$	$1.02095 \pm .00003$

Electromotive-force Measurements

The cells were allowed to age for over a month at 25° before the final measurements were made. Preliminary measurements showed that they changed very little during that time. Measurements were then made successively at 25°, 35°, 40°, 45°, 40°, 35°, 15°, and finally at 25° again. At each temperature measurements were made on successive days until it was shown that equilibrium had been attained. At the higher temperatures equilibrium was attained within less than a day after the temperature was changed. At equilibrium measurements nearly always agreed within 1 or 2 microvolts. The results are given in Tables I, II and III.

The first values at 25° for the unsaturated cells are given in Table I, each value being the average of a group of 5 cells. The figures for the average variation from the group averages give an idea as to the reproducibility of acid cells. In the case of the normal cells, in which there were no variations due to concentration differences, the average variation was

¹¹ The lead wires to the potentiometer were attached to these rods by means of spring clips.

¹² Preliminary experiments showed that weighing after the first heating gave erratic results, due doubtless to loss of sulfur trioxide. It was considered necessary, however, for the expulsion of all the water. See Baxter and Wilson, This Journal, 43, 1238 (1921).

considerably less, 0.000002_{9} volts at 25° . No cells were rejected for inconstancy or disagreement with the majority.¹⁸

TABLE II

		NORMAL CELLS					
Temp., °C	3.	15.00	24.98	35.03	40.03	45.04	
E.m.f., Cells	1-5, volts	1.018456	1.018053	1.017492	1.017167	1.01682	
E.m.f.,	6-10,	1.018450	1.018052	1.017490	1.017164	1.01681	
E.m.f.,	11–15,		1.018056	1.017491	1.017163	1.01681	
E.m.f., Calc.	(Wolff),	1.018459	(1.018054)	1.017488	1.017164		

In Table II it is shown that the temperature formula of Wolff¹⁴ expresses the relationship between temperature and electromotive force of Cells 1 to 15.¹⁵ The practically negligible differences from the calculated values in Table II are in the direction of a smaller temperature coefficient. The results in Table II indicate that mercurous sulfate No. 1, which was used in the unsaturated cells, is a normal preparation, since

Table III

Average Electromotive Forces of Unsaturated Cells at Various Temperatures

	15.00° E.m.f.	24.98° E.m.f. Ia	24.98° E.m.f. IIa	35.03° E.m.f. I
Cells	Volts	Volts	Volts	Volts
16-20	1.018236	1.018270	1.018264	1.018295
41 - 45	1.018346	1.018374	1.018367	1.018393
21-25	1.018531	1.018548	1.018541	1.018558
26-30	1.018703	1.018711	1.018704	1.018709
31–35	1.018784	1.018788	1.018783	1.018784
36-40	1.018991	1.018983	1.018978	1.018968
46-5 0	1.019369	1.019343	1.019334	1.019305
51-55	1.019734	1.019688	1.019679	1.019631
56-60	1.02108	1.02095	1.02095	1.02082
	35.03°	40.03°	40.03°	45.04°
	E.m.f. II	E.m.f. I	E.m.f. II	E.m.f.
Cells				
Cells 16–20	E.m.f. II	E.m.f. I	E.m.f. II	E.m.f.
	E.m.f. II Volts	E.m.f. I Volts	E.m.f. II Volts	E.m.f. Volts
16-20	E.m.f. II Volts 1.018292	E.m.f. I Volts 1.018320	E.m.f. II Volts 1.018318	E.m.f. Volts 1.018359
16-20 41-45	E.m.f. II Volts 1.018292 1.018389	E.m.f. I Volts 1.018320 1.018415	E.m.f. II Volts 1.018318 1.018413	E.m.f. Volts 1.018359 1.018450
16–20 41–45 21–25	E.m.f. II Volts 1.018292 1.018389 1.018554	E.m.f. 1 Volts 1.018320 1.018415 1.018574	E.m.f. II Volts 1.018318 1.018413 1.018572	E.m.f. Volts 1.018359 1.018450 1.018603
16-20 41-45 21-25 26-30	E.m.f. II Volts 1.018292 1.018389 1.018554 1.018707	E.m.f. 1 Volts 1.018320 1.018415 1.018574 1.018720	E.m.f. II Volts 1.018318 1.018413 1.018572 1.018721	E.m.f. Volts 1.018359 1.018450 1.018603 1.018746
16-20 41-45 21-25 26-30 31-35	E.m.f. II Volts 1.018292 1.018389 1.018554 1.018707 1.018781	E.m.f. I Volts 1.018320 1.018415 1.018574 1.018720 1.018793	E.m.f. II Volts 1.018318 1.018413 1.018572 1.018721 1.018793	E.m.f. Volts 1.018359 1.018450 1.018603 1.018746 1.018815
16-20 41-45 21-25 26-30 31-35 36-40	E.m.f. II Volts 1.018292 1.018389 1.018554 1.018707 1.018781 1.018965	E.m.f. I Volts 1.018320 1.018415 1.018574 1.018720 1.018793 1.018971	E.m.f. II Volts 1.018318 1.018413 1.018572 1.018721 1.018793 1.018970	E.m.f. Volts 1.018359 1.018450 1.018603 1.018746 1.018815 1.018988
16-20 41-45 21-25 26-30 31-35 36-40 46-50	E.m.f. II Volts 1.018292 1.018389 1.018554 1.018707 1.018781 1.018965 1.019301	E.m.f. I Volts 1.018320 1.018415 1.018574 1.018720 1.018793 1.018971 1.019300	E.m.f. II Volts 1.018318 1.018413 1.018572 1.018772 1.018793 1.018970 1.019296	E.m.f. Volts 1.018359 1.018450 1.018603 1.018746 1.018815 1.018988 1.019303

^a I and II indicate the first and second results at the given temperature, respectively.

¹⁸ Compare Shaw and Reilley, Trans. Roy. Soc. Canada, [iii] 13, 171 (1919).

¹⁴ Wolff, Bur. Standards Bull., 5, 326 (1908).

¹⁵ The values for Cells 11–15 are the results of the first measurements at 25°, 35°, 40° and 45°. Hysteresis interfered when the temperature was decreased. Cells 1 to 10 and the unsaturated cells showed very little hysteresis.

the saturated cells made with it agree with those made with the other mercurous sulfate preparations. 16

Temperature Coefficients of Unsaturated Cells

There is an average difference of 7 microvolts between the first and second results at 25° in Table III. Smaller differences are to be noticed between the two series of results at 35° and 40°, respectively. These differences may have been caused by a decrease in electromotive force of the cells due to the reaction, $Cd + 2Hg^+ \longrightarrow Cd^{++} + 2Hg$, at the surface of the amalgam, the mercurous ion being supplied by diffusion. ¹⁷ In view of the small size of the decrease and the order in which the measurements at the different temperatures were made, it was considered sufficient

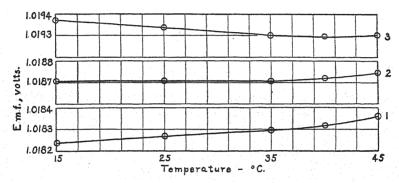


Fig. 2.—Variation of electromotive force with temperature

correction for this error to use the mean values at each temperature for the comparison. The results at 15° were obtained just previous to the final ones at 25°, and so were corrected for comparison with the others by adding half the differences between the two results at 25°. The relation between electromotive force and temperature is shown graphically in Fig. 2. Curve 1 represents the average electromotive force of cells 16–20, Curve 2 that of Cells 26–30, and Curve 3 that of Cells 45–50. Curves for the other groups were similar. The electromotive force is a linear function of the temperature 18° between 15° and 35°, but not between 35° and 45°.

Table IV shows that the temperature coefficient of the unsaturated

¹⁶ Lewis and Gibson [This Journal, **39**, 2575 (1917)] and Gerke [*ibid.*, **44**, 1702 (1922)] have called attention to the possibility of differences in free energy between salts prepared by chemical and electrolytic methods, respectively.

¹⁷ After the final measurements at 25° the unsaturated cells were kept at 25° for 3 months, at room temperature for 3 months more, and then measured at 25°. The average decrease was 23 microvolts, or 0.0023%. The normal cells decreased 6 microvolts during the first 2 months and remained constant for the next 4 months.

¹⁸ Callender and Barnes [*Proc. Roy. Soc.* (London) **62**, 117 (1898)] and Jaeger (Ref. 1, p. 69) found the electromotive force of the unsaturated form of the Clark cell to be a linear function of the temperature over a wide range.

cell is not only "negligible," but at a particular cadmium sulfate concentration is zero between 15° and 35°. This is illustrated in Fig. 3 in which the straight line, expressing the relation between the electromotive

TABL	EIV
TEMPERATURE	COEFFICIENTS

		ATTE TATELLE CALCUT			
Cells	E.m.f. 25° Volts	$\Delta E/\Delta T$ 15-25° Mmv./deg.	$\Delta E/\Delta T$ 25-35° Mmv./deg.	$\Delta E/\Delta T$ 35–40° Mmv./deg.	$\Delta E/\Delta T$ $40-45^{\circ}$ Mmv./deg.
16-20	1.01827	2.8	2.7	5.0	8.1
41-45	1.01837	2.1	2.0	4.7	7.1
21-25	1.01854	1.0	1.1	3.4	5.9
26-30	1.01871	0.1	0.0	2.5	5.4
31-35	1.01879	- 0.1	- 0.3	2.1	4.5
36-40	1.01898	- 1.3	-1.4	0.7	3.5
46-50	1.01934	-3.5	- 3.6	-0.9	0.9
51-55	1.01968	-5.5	- 5.5	-3.2	-0.6
56-60	1.0210	-13	-13	-10	-8

force of the cell and its temperature coefficient, crosses the axis when the electromotive force is 1.01873 volts. The average variation of the temperature coefficients of the individual cells from the values given was about 0.1 microvolts per degree for the temperature coefficients between 15°

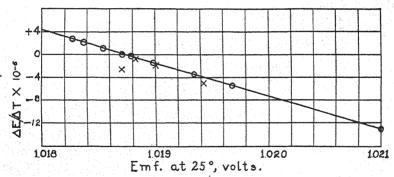


Fig. 3.—Variation of temperature coefficient with electromotive force. The circles represent the acid cells, and the crosses the neutral cells. (See below)

and 35° and about 0.2 mmv. per degree for the other temperature coefficients.

The temperature coefficients between 25° and 35° were measured again after the cells were about 8 months old. The electromotive forces had decreased 17 a little, but the temperature coefficients, in all cases but one, came within 0.2 microvolts per degree of the curve of Fig. 3. The average temperature coefficient of Cells 46–50 was —2.5 mmv. per degree instead of —3.3 as read from the curve, and the agreement among the individual cells was not as good as before. None of the unsaturated cells showed any appreciable hysteresis when the temperature was changed.

Cells with Neutral Electrolyte

Some unsaturated cells with neutral electrolytes were prepared in order to determine if possible how much effect acid in the electrolyte had on the temperature coefficient. The materials were the same as those used in the other cells. The acid in 4 of the cadmium sulfate solutions was neutralized by means of cadmium oxide precipitated from a cadmium sulfate solution by means of ammonium hydroxide, and well washed. Four groups of 5 cells each were prepared and the electromotive forces measured at 25° and at 35°. The temperature coefficients thus obtained did not lie on a straight line or on any regular curve when plotted against electromotive force, as seen in Fig. 3. The temperature coefficient of one group was practically on the curve for the acid cells, but the coefficients of the other groups were below it. Two determinations of the temperature coefficients about a month apart, and before the cells were 3 months old, gave closely agreeing values for 3 of the groups, but for the cells of the average electromotive force of 1.01870 volts the first determination gave —1.5 mmv, per degree, and the second -2.4 mmy, per degree. The latter cells showed considerable hysteresis when the temperature was reduced. Most of the other neutral cells showed some hysteresis. It seems likely that some disturbing factor, such as hydrolysis of the mercurous sulfate, was present in varying degree in the neutral cells and absent in the acid cells.

Electromotive Force and Cadmium Sulfate Concentration

The cadmium sulfate concentrations of the electrolytes of the unsaturated cells are given in Table I. When the concentrations are plotted against the electromotive force of the corresponding cells, all the points, except that for Solution 9, the most dilute one, lie on a straight line. The concentration in a cell having the electromotive force of the normal cell at a certain temperature gives the solubility of hydrated cadmium sulfate in a 0.015~M sulfuric acid solution at that temperature. By plotting the concentrations given in Table I against the electromotive forces at 15° , 18° and 25° , the solubilities calculated as percentages of anhydrous cadmium sulfate were found to be 43.08%, 43.14%, and 43.32%, respectively, the last value requiring a short extrapolation. These values are 0.13%, 0.13% and 0.12% lower, respectively, than the values given by Steinwehr¹⁹ for neutral solutions.

A cell with a zero temperature coefficient, which would have an electromotive force of 1.01873 volts, would require an electrolyte containing 42.93% cadmium sulfate. If the effect of acid on the solubility of cadmium sulfate is the same at lower temperatures as between 15° and 25° the electrolyte of the cell with zero temperature coefficient would be saturated at the same temperature as a 43.06% neutral solution, namely at about 4°.

¹⁹ Steinwehr, Z. physik. Chem., 94, 6 (1920).

Differential Heat of Solution of Cadmium Sulfate

The differential heat of solution of hydrated cadmium sulfate in its saturated solution, q', can be calculated by means of the equation²⁰

$$q' = 46148 \frac{m - 2.67}{m} T_0 \left[\frac{dE_1}{dT} - \frac{dE_2}{dT} \right]$$

where m is the number of moles of water per mole of cadmium sulfate in the saturated solution, E_1 is the electromotive force of the normal cell, E_2 that of a cell with saturated electrolyte but without crystals, and T_0 is the temperature. The results of this calculation are given in Table V. The temperature coefficients for the normal cell were obtained by differentiating Wolff's formula, 14 and those for the cells without crystals from curves similar to Fig. 3 drawn for the temperatures 15° , 18° and 25° . The values of m were calculated from the solubilities given above of hydrated cadmium sulfate in a 0.015 M sulfuric acid solution.

Table V

Differential Heat of Solution of Hydrated Cadmium Sulfate in a Saturated Solution Containing 0.012 Mole of Sulfuric Acid in a Liter

Temp.	m Moles	dE_1/dT Volts/deg.	dE_2/dT Volts/deg.	Cal./mole
15	15.27	-0.00003057	0.00000153	-352
18	15.23	00003686	.00000205	-431
25	15.12	00004945	.00000392	-605

If it is assumed that the temperature coefficient of neutral unsaturated cells is the same as for the acid ones of the same electromotive force, the heats of solution in Table V apply to neutral solutions as well as to the slightly acid ones for which they were calculated. For neutral solutions the values for dE_1/dT would be the same, since Wolff's formula, although derived for neutral cells, has been shown to hold for the acid cells. The values of m would be 3 to 4 parts in a thousand lower for neutral solutions, but an examination of the above equation shows that the values of q' would be in error by only a small part of this.

The differential heat of solution at 18° as determined in the above manner is less than half the value found by Steinwehr²¹ by a different method. The temperature coefficient of q' in the vicinity of 18° is -25 cal. per degree according to the above results while Steinwehr¹⁹ calculated -63 to -78 cal. per degree.

Summary

- 1. The electromotive force of unsaturated Weston cells increased in an approximately linear manner as the cadmium sulfate concentration decreased.
- 2. The electromotive forces were linear functions of the temperatures between 15° and 35° but were not linear functions between 35° and 45°.
 - ²⁰ Jaeger, Ref. 1, p. 36. Verhdl. Deutsch. Phys. Ges., 3, 50 (1901). Ref. 19, p. 14.
 ²¹ Steinwehr, Z. physik. Chem., 88, 245 (1914).

- 3. The temperature coefficient between 15° and 35° was found to be a linear function of the electromotive force. It decreased from 0.0000028 volts per degree for cells with an electromotive force of 1.01827 volts to —0.000013 volts per degree for cells with an electromotive force of 1.0210 volts, being zero for a cell with an electromotive force of 1.01873 volts.
- 4. Normal cells with electrolytes made by saturating a $0.015\ M$ sulfuric acid solution with hydrated cadmium sulfate behaved in accordance with Wolff's temperature formula.
- 5. Mercurous sulfate prepared by reduction of mercuric sulfate with formaldehyde at 100° was no different in its behavior in normal cells from the electroltyic salt.
- 6. The differential heat of solution of hydrated cadmium sulfate in a slightly acid saturated solution was calculated.

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THE ENTROPY OF DIATOMIC GASES AND ROTATIONAL SPECIFIC HEAT

By Richard C. Tolman and Richard M. Badger Received July 3, 1923

I. Introduction

Assuming the rigid "dumb-bell" model, the entropy of a diatomic gas at temperatures high enough so that the specific heat at constant pressure has become $7/2\ R$, is given by the equation

$$S = \frac{7}{2} R \ln T - R \ln p + \frac{3}{2} R \ln M + R \ln J + S_2$$
 (1)

where T is the absolute temperature, p is the pressure, M the molecular weight, J the moment of inertia of the molecule and S_2 a constant which has the same value for all diatomic gases composed of molecules of the assumed model. This equation has been derived by Tetrode, Sackur and Schames on the basis of the quantum theory and by Tolman from the theory of similitude or relativity of size, and using kinetic-theory data for calculating moments of inertia, has been shown to agree with the available experimental data.

An important advance in the use of Equation 1 has been made by Urey.⁵ In the first place he has used moments of inertia obtained from spectral data instead of kinetic-theory data in testing the equation,⁶ and in the

- ¹ Tetrode, Ann. Physik, 38, 434 (1912).
- ² Sackur, ibid., 40, 87 (1913).
- ³ Schames, Physik. Z., 21, 38 (1920).
- 4 Tolman, THIS JOURNAL, 43, 866 (1921).
- ⁵ Urey, ibid., 45, 1445 (1923).
- ⁶ Compare also Eucken, Jahrb. Radioakt. Elektronik, 16, 361 (1920); Z. Elektrochem. 26, 377 (1920).

second place he has obtained a theoretical value for the constant S_2 by making use of one of Reiche's equations for the rotational specific heat of diatomic gases. This latter possibility is of great interest since the work of Tetrode, Sackur and Schames did not make the theoretical value of this constant by any means certain, while the theory of the relativity of size gives no information as to the theoretical value of the constant.

Urey's method for determining the constant S_2 involved a laborious calculation of the whole rotational specific-heat curve from the absolute zero to a temperature where the rotational specific heat is approximately equal to R, followed by a graphical integration under this curve to determine the rotational entropy at the higher temperature, and was applied to only one of the several theoretical formulas for rotational specific heat which have been proposed. It is the purpose of the present article to show a simple mathematical method for obtaining the value of S_2 from various theoretical formulas for rotational specific heat, to apply the method to the 5 different formulas considered by Reiche⁷ and to the new formula based on half-quantum numbers recently considered by Tolman, and to compare the results obtained with the available experimental data.

II. The Additivity of Translational and other Forms of Entropy

The calculations presented in this article will be based on the assumption that the entropy of a gas can be calculated by putting it equal to the sum of the entropy given by the Sackur⁹ equation, which it would have as a perfect monatomic gas, plus the additional quantity of entropy which corresponds to the increase in the value of the specific heat C_p over 5/2 R as we proceed up from the absolute zero; in other words, that the total entropy is given by the equation

$$S = {}^{5}/{}_{2}R\ln T - R\ln p + {}^{3}/{}_{2}R\ln M + S_{1} + \int_{0}^{T} (C_{p} - {}^{5}/{}_{2}R) \frac{dT}{T}$$
 (2)

The above hypothesis was proposed by Tolman¹⁰ and found to be correct within the probable limits of experimental knowledge for the case of the entropy of diatomic hydrogen at 25° using actual specific-heat data for the evaluation of the last term in Equation 2. No claim is made as to the theoretical justification for this hypothesis. An equivalent hypothesis was earlier employed by Langen¹¹ for the calculation of Nernst's chemical constants, making use, however, of the theoretically incorrect Einstein-Stern equation for the specific heat of diatomic gases.

⁷ Reiche, Ann. Physik, 58, 657 (1919).

⁸ Tolman, "Rotational Specific Heat and Half Quantum Numbers," to appear shortly in the *Physical Review*.

⁹ Sackur, Ann. Physik, 36, 968 (1911); 40, 67 (1913).

¹⁰ Tolman, This Journal, 42, 1185 (1920).

¹¹ Langen, Z. Elektrochem., 25, 25 (1919).

III. General Equation for Rotational Specific Heat

Except for the case of diatomic hydrogen, we have no experimental specific-heat data that would permit the direct evaluation of the last term in Equation 2 and must resort to some theoretical expression for calculating the excess specific heat due to the rotation of our "dumb-bell" molecules.

For convenience let us define the quantities Q and σ by the equations

$$Q = \sum p_m e^{-m^2 \sigma} \tag{3}$$

and

$$\sigma = \frac{h^2}{8\pi^2 JkT} \tag{4}$$

where p_m is the a-priori probability that a molecule will have the azimuthal quantum number m, J is the moment of inertia of the rigid "dumb-bell" molecule, h, k, and T have their usual significance and the summation Σ is to be taken over all the possible rotational states. It can then easily be shown that the rotational specific heat is given by the equation

$$C_R = R \sigma^2 \frac{d^2 \ln Q}{d \sigma^2} \tag{5}$$

IV. Integration between Zero and T

With the help of Equation 5 we obtain for the rotational entropy at temperature T the expression

$$S_R = \int\limits_0^T R \,\sigma^2 \frac{d^2 \ln Q}{d \,\sigma^2} \,d \ln T$$

Introducing the relation between σ and T given by Equation 4, we can transform the above expression as follows,

$$S_{R} = -\int_{0}^{T} R \sigma^{2} \frac{d^{2} \ln Q}{d \sigma^{2}} d \ln \sigma = R \left[\ln Q - \sigma \frac{d \ln Q}{d \sigma} \right]_{0}^{T}$$

$$= R \left(\ln Q_{T} - \sigma_{T} \frac{d \ln Q_{T}}{d \sigma} - \ln Q_{0} + \sigma_{0} \frac{d \ln Q_{0}}{d \sigma} \right)$$
(6)

Since the different theories of specific heat usually lead to simple expressions for $\ln Q$ at very low temperatures and at temperatures high enough so that the rotational specific heat has become R, the above expression for rotational entropy can easily be evaluated in the cases of interest without the necessity of determining the whole specific-heat curve.

V. Values of Q Given by Different Theories

Different hypotheses as to the value of the lowest possible azimuthal quantum number, and as to the relation between quantum number and a-priori probability have led to different expressions for Q. The following expressions for Q will be tested in this paper,—

I.
$$Q = \sum_{0}^{\infty} (2m+1)e^{-m^2\sigma}$$
 IV. $Q = \sum_{1}^{\infty} (m+1)e^{-m^2\sigma}$ II. $Q = \sum_{0}^{\infty} (m+1)e^{-m^2\sigma}$ V. $Q = \sum_{1}^{\infty} 2m e^{-m^2\sigma}$ III. $Q = \sum_{1}^{\infty} (2m+1)e^{-m^2\sigma}$ VI. $Q = \sum_{1}^{\infty} 2n e^{-(n-1/2)^2\sigma}$

The first five of these expressions are the ones which were derived by Reiche⁷ on the basis of the first form of quantum theory and different assumptions as to the lowest quantum number and as to a-priori probabilities, and the sixth is the one discussed by Tolman8 derived on the new assumption that the lowest possible azimuthal quantum number is 1/2. A statement of the hypotheses which have led to these different expressions for Q will be found in the paper of Tolman.8 The expressions I and II are intrinsically not very probable since they lead to specific-heat curves with maxima at temperatures lower than the final asymptotic approach to the value R.

Evaluation of Rotational Entropy

We may now evaluate the rotational entropy as given by Equation 6 for the above six cases.

Case I. $Q = \sum_{n=0}^{\infty} (2m+1)e^{-m^2\sigma}$. At high temperatures we may evidently write the approximations

$$Q_T = \int_0^\infty (2 m + 1)e^{-m^2\sigma} dm = \frac{1}{\sigma_T} \left(1 + \frac{1}{2} \sqrt{\pi \sigma_T} \right)$$

$$\ln Q_T = -\ln \sigma_T + \frac{1}{2} \sqrt{\pi \sigma_T}, \text{ and } \frac{d \ln Q_T}{d \sigma} = -\frac{1}{\sigma_T} + \frac{1}{4} \sqrt{\frac{\pi}{\sigma_T}}$$

and at low temperatures the approximations

$$Q_0 = 1 + 3 e^{-\sigma_0}$$
, $\ln Q_0 = 3 e^{-\sigma_0}$ and $\frac{d \ln Q_0}{d \sigma} = -3 e^{-\sigma_0}$

Substituting into Equation 6, for the rotational entropy at temperature T, we obtain

$$S_R = R(-\ln \sigma_T + \frac{1}{2}\sqrt{\pi\sigma_T} + 1 - \frac{1}{4}\sqrt{\pi\sigma_T} - 3e^{-\sigma_0} - 3\sigma_0e^{-\sigma_0})$$

Returning now to Equation 4 by which σ was defined $\sigma = \frac{h^2}{8\pi^2 T h T}$

$$\sigma = \frac{h^2}{8\pi^2 Ik7}$$

we see that σ approaches zero at high temperatures and infinity at low temperatures so that for the case in which we are interested we have

$$S_R = R \ln T + R \ln J + R \ln \frac{8 \pi^2 k}{h^2} + R$$
 (7)

and substituting S_R for $\int_0^1 (C_p - \frac{5}{2}R) d \ln T$ in Equation 2 we obtain for the total entropy of our diatomic gas

$$S = {}^{7}/{}_{2}R\ln T - R\ln p + {}^{3}/{}_{2}R\ln M + R\ln J + \left(S_{1} + R\ln \frac{8\pi^{2}k}{h^{2}} + R\right)$$
 (8)
where
$$S_{2} = S_{1} + R\ln \frac{8\pi^{2}k}{h^{2}} + R$$
 (9)

is the constant of the entropy equation.

Since Reiche⁷ and Tolman⁸ have given simple values for In Q at high and low temperatures for the other theories of rotational specific heat,

an entirely similar method of calculation can be used for evaluating the constants, using the other forms of Q that have been proposed. The results are given in Table I.

The second column gives the form of Q that has been considered and the third column the form found for S_2 . Expressing entropies in calories per degree per mole, pressure in atmospheres, molecular weight in grams per mole, moment of inertia in grams cm. squared per mole, and using Lewis'12 value, -2.63, for S_1 , we have calculated the numerical values of S_2 given in the fourth column.

Since we shall generally be interested in the value for the entropy of gases at 1 atmosphere pressure and 25° C. = 298.1° K., we may substitute these values of pressure and temperature in Equation 1 and rewrite it in the form

$$S_{298.1}^{\circ} = \sqrt[3]{2R \ln M} + R \ln J + C_{298.1}$$
 (10)

Numerical values of C_{298-1} are given in the last column of Table I.

TABLE I

	Sum	mary of Results		
Case	Form of Q	Form of S_2	S_2	C298.1
Ι	$\sum_{0}^{\infty} (2 m + 1)e^{-m^2\sigma}$	$S_1 + R \ln \frac{8 \pi^2 k}{h^2} + R$	66.30	105.95
II	$\sum_{0}^{\infty} (m+1)e^{-m^2\sigma}$	$S_1 + R \ln \frac{8 \pi^2 k}{h^2} + R - R \ln 2$	64.92	104.57
III	$\sum_{1}^{\infty} (2 m + 1)e^{-m^2\sigma}$	$S_1 + R \ln \frac{8 \pi^2 k}{h^2} + R - R \ln 3$	64.12	103.77
IV	$\sum_{1}^{\infty} (m+1)e^{-m^2\sigma}$	$S_1 + R \ln \frac{8\pi^2 k}{h^2} + R - 2R \ln 2$	63.54	103.19
V	$\sum_{1}^{\infty} 2 m e^{-m^2 \sigma}$	$S_1 + R \ln \frac{8 \pi^2 k}{h^2} + R - R \ln 2$	64.92	104.57
vi	$\sum_{1}^{\infty} 2 n e^{-(n-1/2)^2 \sigma}$	$S_1 + R \ln \frac{8 \pi^2 k}{h^2} + R - R \ln 2$	64.92	104.57

VII. Discussion of the Different Values of S2

It will be noticed that three of the proposed theories of specific heat (II, V and VI) have led to the same value of S_2 . Of these, Theory II is not entirely probable since it is based on the assumption that a-priori probabilities are to be calculated by counting positive and negative rotations only once, which does not agree with the Bohr correspondence principle. Theory V is perhaps as probable as any of those based on the assumption that the lowest possible azimuthal quantum number is unity, and Theory VI is the one based on the assumption that the lowest possible azimuthal quantum number is $^{1}/_{2}$.

Theory V is the one selected by Urey⁵ for determining S₂ by graphical ¹² Lewis, *Phys. Rev.*, **18**, 121 (1921). See also Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 457.

integration under the specific-heat curve. Urey obtained in this way a value which, using our method of expression, 13 gives $S_2 = 64.93$, while we have obtained by a more direct mathematical treatment the practically identical value, $S_2 = 64.92$.

Since the different theoretical values for S_2 differ among themselves by a maximum of less than 3 cal./mole deg., an experimental decision as to the correct value for S_2 is difficult. Accurate values for the entropy and moment of inertia are both needed, the possible deviation from the assumed rigid "dumb-bell" model must be considered, and the assumption that the specific-heat curve has already reached the value $C_p = 7/2$ R must be scrutinized.

Moments of inertia calculated from the *classical* formula for the wave lengths of the maxima of infra-red double bands

$$J = kT \left\{ \frac{\lambda_1 \lambda_2}{\pi c (\lambda_2 - \lambda_1)} \right\}^2$$

are evidently less suitable for exact tests than those calculated on the basis of the quantum theory from a complete knowledge of the rotation spectrum, and moments of inertia calculated on the basis of the quantum theory from band or many-lined spectra in the visible or ultraviolet are not completely satisfactory since they presumably correspond to the molecule in an excited condition rather than in the normal condition which contributes to specific heat at moderate temperatures.

The following table presents all the figures for the calculated and experimental values of the entropy of diatomic gases at $25\,^{\circ}$ C. and 1 atmosphere that we have felt justified in including. The data upon which some of the figures are based are far from satisfactory, as will be indicated in the discussion that follows. Hydrogen has been omitted since the specific heat is still considerably below 7/2 R at $25\,^{\circ}$, and the moment of inertia would have to be obtained from the many-lined spectrum that corresponds to an excited condition of the molecule. Carbon dioxide and hydrogen cyanide have been included since the spectral data for these substances indicate that the structure of the molecule is linear and that they behave like rigid diatomic molecules.

The first column of the table gives the formula of the substance, the second column the value of the moment of inertia in grams cm. squared which was used for the calculation, the third column the experimental value of the entropy as determined by thermodynamic methods, and the remaining columns the values of the calculated entropies using the six different formulas developed in this paper, together with the deviations from the experimental values. The values of entropy calculated by the three formulas II, V and VI which agree have been put in a single column.

¹³ Urey used volumes instead of pressures in his entropy equation. It is easy to show that the constants for the two methods of expression differ by $R \ln R$.

The values of the moments of inertia for the first four gases in Table II are the ones used by Urey.⁵ The value for hydrogen chloride is based on Ime's data for the infra-red bands and hence is very accurate. The value for nitrogen is from the constant 2B for the 3883 cyanogen band as given by Kratzer, and hence suffers from the grave doubt as to whether this band is due to nitrogen or cyanogen. The values for carbon monoxide and nitric oxide are calculated by the classical formula from the separation of the maxima of infra-red bands and hence are not exact.

S	ubstance	J×1040	S exptl.	$\mathcal{S}_{\mathtt{I}}$	Dev.	$\mathcal{S}_{ ext{III}}$	Dev.	S_{IV}	Dev.	SII, V, VI Dev.
	HCl -	2.594	43.3	44.3	1.0	42.1	1.2	41.6	1.7	42.9 0.4
	N_2	14.4	45.6	46.9	1.3	44.8	0.8	44.2	1.4	45.6 0.0
	CO	14.7	45.6	47.0	1.4	44.8	0.8	44.2	1.4	45.6 0.0
	NO	14.3	49.3	47.1	2.2	45.0	4.3	44.4	4.9	45.8 3.5
	CO ₂	50	49.4	50.8	1.4	48.6	0.8	48.0	1.4	49.4 0.0
	HCN	33	49.1	48.9	0.2	46.3	2.8	45.7	3.4	47.1 2.0

The treatment of carbon dioxide is based on the assumption that this behaves like a diatomic gas with the carbon atom in the middle between the oxygen atoms. The moment of inertia is that obtained by Barker¹⁴ from infra-red spectra, who concludes from the spectral data that the molecule is linear in structure rather than triangular. It is a matter of great interest that the inverse calculation of the moment of inertia of carbon dioxide from thermodynamic data was made by Eucken,¹⁵ before Barker's results were known. Eucken in his calculations used the language of Nernst's chemical constants rather than that of entropy and used what was equivalent to an empirical rather than a theoretical value for the constant S_2 . He obtained the value for carbon-dioxide $J=50\times 10^{-40}$ g. cm. squared in complete agreement with the later spectral work of Barker who was himself unfamiliar with Eucken's work, which had appeared only a few months earlier.

Hydrogen cyanide is also treated as a rigid linear structure. The moment of inertia has been calculated from the separation between the maxima $\lambda_1=13.60\mu$, and $\lambda_2=14.33\,\mu$ measured by Burmeister. The spectral data now available show no evidence of a third moment of inertia. If we assume radii for the atoms that are consistent with those found for these same atoms in other gases, it seems necessary to assume that the hydrogen atom is between the carbon and nitrogen atoms in order to account for the large moment of inertia, $J=33\times13^{-40}$. The assumption of such a structure is undoubtedly bizarre but finds some support from the theory of hydrogen bonds proposed by Latimer and Rodebush. ¹⁷

¹⁴ Barker, Astrophys. J., 55, 391 (1922).

¹⁵ Eucken, Z. physik. Chem., 100, 159 (1922).

¹⁶ Burmeister, Verh. D. phys. Geo., 15, 589 (1913).

¹⁷ Latimer and Rodebush, This Journal, 42, 1431 (1920).

The experimental values of the entropies of the diatomic gases are those given by Eastman.¹⁸ The experimental values for the triatomic gases have been calculated from the free-energy data of Lewis and Randall.¹⁹ The values for nitric oxide and hydrogen cyanide may be greatly in error owing to the insufficiency of the thermodynamic data.

It would be dangerous to draw from the figures in Table II an absolutely definite conclusion as to the correct theory of rotational specific heat and rotational entropy. The derivations assumed are (1) a rigid dumb-bell molecule whose moment of inertia does not change with speed of rotation, (2) rotational energy for the molecule but no vibrational energy, (3) a specific-heat curve that has already reached 7/2 R at the temperature in question. Our spectral knowledge of hydrogen chloride is enough to tell us that Conditions 1 and 2 will be nearly met by this molecule, but the assumption that the specific heat is already 7/2 R is not justified for this gas at 25°C., owing to the small value of J. Nitrogen must be excluded for an exact test owing to the probability that the bands used belong to evanogen rather than nitrogen. Carbon monoxide and nitric oxide are unsuitable for exact tests since their moments of inertia had to be calculated from the classical formula. Furthermore, the experimental value for the entropy of nitric oxide may be greatly in error. Carbon dioxide is not suitable since the value of the specific heat is apparently already greater than 7/2 R at 25°. Finally, in the case of hydrogen cyanide both the spectral data and the thermodynamic data are unsatisfactory.

In spite of these difficulties, we feel that the tentative conclusion may be drawn in favor of the rotational entropy given alike by Theories II, V and VI. If we eliminate nitric oxide and hydrogen cyanide where the experimental values of the entropy may be greatly in error, we note an almost perfect correspondence between the experimental entropy and the value given by Theories II, V and VI. Under all the circumstances it would seem best to use for the present the values of S_2 and C_{298-1} , given by these theories.

VIII. Summary

1. A direct mathematical method has been developed for determining the theoretical values of the constants S_2 and C_{298-1} in the equations for the entropy of diatomic gases,

$$S = \frac{7}{2} R \ln T - R \ln p + \frac{3}{2} R \ln M + R \ln J + S_2$$

$$S(298.1^{\circ}, 1 \text{ atm.}), = \frac{3}{2} R \ln M + R \ln J C_{298.1}$$

- 2. Six different theories which have been proposed for rotational specific heat all based on the first form of quantum theory, but based on different theories as to a-priori probabilities and as to the lowest possible
 - 18 Eastman, This Journal, 45, 80 (1923).
- ¹⁹ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.

azimuthal quantum number, have been used to determine the theoretical values of S_2 and $C_{298.1}$ and the results compared with experimental values.

3. In the absence of further evidence, the best values for S_2 and $C_{298.1}$ are 64.92 and 104.57, respectively. (Entropy in calories, temperature in degrees centigrade absolute, pressure in atmospheres, molecular weight in grams per mole, moment of inertia in gram cm. squared per mole.)

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THE TEMPERATURE COEFFICIENT OF PHOTOCHEMICAL REACTION RATE

By Richard C. Tolman Received July 9, 1923

I. Introduction

Let us consider a photochemical reaction, $aA + bB + \ldots \longrightarrow Products$, taking place at some given temperature T, under the influence of radiation from an external source, the frequency of the radiation being ν , and its energy density throughout the reacting mixture being u_{ν} . If we confine our attention to cases where the rate of reaction is proportional to the energy density u_{ν} and where the law of Guldberg and Waage is followed, we may write for the rate of the above reaction the expression,

$$-\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t}=k_{\nu}u_{\nu}C_{\mathrm{A}}^{\mathrm{a}}C_{\mathrm{B}}^{\mathrm{b}}\ldots \tag{1}$$

The quantity k_{ν} occurring in Equation 1 may be called the *specific photochemical reaction rate*. It is the rate at which the reaction would proceed if the reacting substances were present at *unit concentration* and subjected to radiant energy of frequency ν and *unit energy density*. The quantity k_{ν} is a parameter, independent of the concentration and energy density, but dependent on the temperature T and frequency ν . The temperature T is to be taken as that which would exist if the illumination from the external source were cut off. It is the purpose of the following article to present a theoretical treatment of the change in k_{ν} with T.

In an earlier article, ¹ the writer has already shown that for a monomolecular photochemical reaction, the temperature coefficient of photochemical reaction rate will be given by the equation

$$\frac{\partial \ln k_{\nu}}{\partial T} = \frac{\bar{\epsilon} - \bar{\epsilon}}{kT^2} \tag{2}$$

where $\bar{\epsilon}$ is the average energy of the molecules which pick up radiant energy and react, $\bar{\epsilon}$ is the average energy of all the molecules and k is Boltzmann's constant. In the article referred to, the above equation

¹ Tolman, This Journal, 42, 2506 (1920).

was obtained as a result which was incidental to a treatment of thermal reaction rates, and the methods employed were those of the classical statistical mechanics.

In this article we shall present a simple and direct proof of Equation 2, using the methods of the quantum theory instead of those of the classical statistical mechanics. Consideration will also be given to the temperature coefficient of bimolecular reactions, attention will be paid to the nature of the quantity $\frac{\partial}{\partial \nu} \left(\frac{\partial \ln k_{\nu}}{\partial T} \right)$, an interpretation of existing data on photochemical temperature coefficients will be given, a criticism will be made of Plotnikow's attempted classification of photochemical temperature coefficients into three groups, and some discussion of Einstein's

We may now proceed to our theoretical treatment.

law of photochemical equivalence will be presented.

II. The Number of Molecules in a Given Quantum State

The chance that a molecule will pick up radiant energy and hence undergo a monomolecular change, or in the case of bimolecular reactions arrive in an activated state such as to facilitate reaction upon collision, will evidently depend not only upon the frequency and density of the radiant energy involved but also upon the internal condition or quantum state of the molecule at the time it is subjected to the radiant energy.

For the number of molecules N_i in the i^{th} quantum state we shall use the expression

$$N_{i} = N \frac{p_{i} e^{-\epsilon_{i}/kT}}{\sum_{i} p_{i} e^{-\epsilon_{i}/kT}}$$
(3)

where N is the total number of molecules present, p_i is the a-priori probability that a molecule will be in the i^{th} quantum state, ϵ_i is the energy corresponding to the i^{th} quantum state, k and T have their usual significance and the summation \sum_{0}^{∞} is to be carried out over all possible quantum states of the kind in question.

The justification for this equation rests at the present time largely upon its correspondence with the Maxwell-Boltzmann distribution law, familiar in the classical statistical mechanics, which may be written in the form

$$d N = N \frac{e^{-\epsilon/kT} d\sigma}{\oint e^{-\epsilon/kT} d\sigma}$$
(4)

where ϵ is the energy of a molecule whose coördinates and momenta have values falling in the region $d\sigma$ and the integration \mathcal{I} is to be taken over the whole of the generalized space σ . Equation 4 may be regarded as the limit approached by Equation 3 in the regions of generalized space corresponding to high quantum numbers where the successive energy levels

are near together, the a-priori probabilities p_i occurring in Equation 3 and the size of the infinitesimal regions $d\sigma$ occurring in (4) being chosen so as to secure correspondence between (3) and (4) at the limit, thus satisfying the Bohr correspondence principle. The simplest procedure is to choose the a-priori probabilities as equal to the number of ways² in which a given quantum state can occur, and then adjust the size of $d\sigma$ so as to secure the desired correspondence.

III. Rate of a Monomolecular Photochemical Reaction

We may now proceed directly to obtain an expression for the rate of a monomolecular photochemical reaction. The mechanism of such a reaction may be pictured as consisting in the absorption of a quantum of radiant energy of magnitude $h\nu$ which raises the molecule to such an energy level that the monomolecular change can take place.

Let $\alpha_{i\nu}$ be the chance in unit time that a molecule in the i^{th} quantum state surrounded by radiant energy of frequency ν and unit density will absorb a quantum of energy $h\nu$, and $s_{i\nu}$ be the chance that such an activated molecule will undergo the monomolecular transformation in question. The quantity $s_{i\nu}$ will be unity only in case every activated molecule reacts without losing its activation before reaction by re-emission. Making use of Equation 3 for the number of molecules in the i^{th} quantum state we may then evidently write for the rate at which molecules are reacting under the influence of radiant energy of frequency ν and density u_{ν} the expression,

$$-\frac{\mathrm{d}N}{\mathrm{d}t} = u_{\nu} N \frac{\sum_{i}^{\infty} \alpha_{i\nu} \, p_{i} \, e^{-\epsilon_{i}/kT}}{\sum_{i}^{\infty} p_{i} \, e^{-\epsilon_{i}/kT}}$$
(5)

where the summation \sum_{0}^{∞} is to be taken over all possible states. Noting that $(-dN/dt)/(u_{\nu}N)$ is the quantity which we have called the specific photochemical reaction rate k_{ν} , we may now write,

$$k_{\nu} = \frac{\sum_{i=0}^{\infty} \alpha_{i\nu} s_{i\nu} p_{i} e^{-\epsilon_{i}/kT}}{\sum_{i=0}^{\infty} p_{i} e^{-\epsilon_{i}/kT}}$$
(6)

The above expression for photochemical reaction rate would permit a relatively complete solution of the whole problem of monomolecular photochemical reaction rate if we had sufficient knowledge of the values of $\alpha_{i\nu}$, $s_{i\nu}$, p_i and ϵ_i . At the present stage of scientific development, however, such knowledge is largely lacking. Moreover, at the present time we

² For example, in the case of a rotating molecule of the dumb-bell model this would mean the number of possible distinguishable orientations having the same azimuthal quantum number, as determined from the theory of quantization in space.

have little knowledge of the absolute values of k_{ν} since few photochemical experiments have been made with *monochromatic* light of *known intensity*. For both these reasons we shall find it advisable to turn our main attention to the percentage temperature coefficient of k_{ν} rather than its absolute value, since the theoretical treatment of the temperature coefficient does away for the most part with the necessity of detailed knowledge of the quantities in Equation 6, and there is furthermore a considerable body of data on photochemical temperature coefficients.

IV. Temperature Coefficient of Monomolecular Photochemical Reaction Rate

Assuming the quantities $\alpha_{i\nu}$, $s_{i\nu}$ and p_i independent of the temperature, which is certainly justifiable as a first approximation, we may carry out a logarithmic differentiation of Equation 6 and obtain

$$\frac{\partial \ln k_{\nu}}{\partial T} = \frac{1}{k_{\nu}} \frac{\partial k_{\tau}}{\partial T} = \frac{1}{k_{\nu}} \frac{\sum_{0}^{\infty} \alpha_{i\nu} s_{i\nu} p_{i} e^{-\epsilon_{i}/kT}}{\sum_{0}^{\infty} p_{i} e^{-\epsilon_{i}/kT}} - \frac{\sum_{0}^{\infty} p_{i} e^{-\epsilon_{i}/kT} \frac{\epsilon_{i}}{kT^{2}}}{\sum_{0}^{\infty} p_{i} e^{-\epsilon_{i}/kT}}$$

An examination of the first term on the right hand side of the above equation will show that it is equal to the average energy before activation of the molecules which actually pick up radiant energy and react, divided by kT^2 . The second term is obviously the average energy of all the molecules divided by kT^2 . Hence we may rewrite the above equation in the form

$$\frac{\partial \ln k_{\nu}}{\partial T} = \frac{\overline{\epsilon} - \overline{\epsilon}}{kT^2} \tag{7}$$

where the symbols $\bar{\epsilon}$ and $\bar{\epsilon}$ have the significance explained above.³

Before proceeding to a consideration of the interpretation of experimental facts with the help of this very simple equation, we shall first show that a slightly modified form of Equation 7 will also apply to dimolecular reactions.

V. Rate of a Bimolecular Photochemical Reaction

The mechanism of a bimolecular photochemical reaction may be pictured as consisting in the activation of one or both of the molecules entering into the reaction followed by collision and reaction. Let the reaction in question be $A + B \longrightarrow Products$ and let us consider the case in which only the molecules of A are activated by the extraneous radiation. For

³ The similarity of this equation in form to that for thermal reactions should be noted. In the case of thermal reactions, however, the quantity $\frac{1}{\epsilon} - \frac{1}{\epsilon}$ must be replaced by the whole energy of activation. See Tolman, Ref. 1.

the number of such activated molecules $N_{i\nu}$ present at any given time with the energy

$$\epsilon_{i\nu} = \epsilon_i + h\nu \tag{8}$$

we may evidently write

$$N_{i\nu} = N_{\rm A} \frac{u_{\nu} \alpha_{i\nu} \tau_{i\nu} p_{i} e^{-\epsilon_{i}/kT}}{\sum_{i} p_{i} e^{-\epsilon_{i}/kT}}.$$
(9)

where $N_{\rm A}$ is the total number of molecules of A, $\alpha_{i\nu}$ is the chance per unit time that a molecule in the $i^{\rm th}$ quantum state will pick up a quantum when surrounded by unit energy density of frequency ν , and $\tau_{i\nu}$ is the average life that such an activated molecule exists without reëmission. Furthermore, for the number of molecules of B in the $j^{\rm th}$ quantum state we may write,⁴

$$N_{i} = N_{\rm B} \frac{p_{i} e^{-\epsilon_{i}/kT}}{\sum\limits_{0}^{\infty} p_{i} e^{-\epsilon_{i}/kT}}$$
(10)

The chance that a molecule of A in the quantum state iv will collide with a molecule of B in the quantum state j will evidently be proportional to the product of the concentrations of molecules in these states, and in the case of gases as a first approximation to the square root of the absolute temperature. Hence if we denote by s_{ivj} the chance that reaction will take place on a collision between molecules in these states, we may evidently write with the help of Equations 9 and 10 for the rate of the dimolecular reaction the expression,

$$-\frac{1}{v}\frac{\mathrm{d}N_{\mathrm{A}}}{\mathrm{d}T} = k_{c}T^{1/2}\frac{N_{\mathrm{A}}}{v}\frac{N_{\mathrm{B}}}{v}u_{\nu}\frac{\sum\limits_{0}^{\infty}\sum\limits_{0}^{\infty}\alpha_{i\nu}\tau_{i\nu}s_{i\nu j}p_{i}e^{-\epsilon_{i}/kT}p_{j}e^{-\epsilon_{j}/kT}}{\left(\sum\limits_{0}^{\infty}p_{i}e^{-\epsilon_{i}/kT}\right)\left(\sum\limits_{0}^{\infty}p_{j}e^{-\epsilon_{j}/kT}\right)}$$

where v is the volume of the container, k_c is a constant which determines the number of collisions when the temperature is given, and the summation in the numerator is to be taken over all states i and j. If we again define k_r as the rate of reaction at unit concentrations under the influence of unit energy density we may write

$$k_{\nu} = k_{c} T^{i/2} \frac{\sum_{i=1}^{\infty} \sum_{i=1}^{\infty} \alpha_{i\nu} s_{i\nu j} p_{i} e^{-\epsilon_{i}/kT} p_{j} e^{-\epsilon_{j}/kT}}{\left(\sum_{i=1}^{\infty} p_{i} e^{-\epsilon_{i}/kT}\right) \left(\sum_{i=1}^{\infty} p_{i} e^{-\epsilon_{i}/kT}\right)}$$
(11)

As in the case of monomolecular reactions, we shall find it more informing to consider the temperature coefficient of reaction rate rather than its absolute value and shall proceed to obtain its value.

4 In obtaining Formulas 9 and 10 we assume that the values of $N_{i\nu}$ and $N_{j\nu}$ are not appreciably affected by losses through reaction.

VI. Temperature Coefficient of Bimolecular Photochemical Reaction Rate

Carrying out a logarithmic differentiation of Equation 11 we obtain

$$\frac{\partial \ln k_{\nu}}{\partial T} = \frac{1}{k_{\nu}} \frac{\partial k_{\nu}}{\partial T} = \frac{1}{2T} + \frac{1}{k_{\nu}} k_{c} T^{1/2} \frac{\sum\limits_{0}^{\infty} \sum\limits_{0}^{\infty} \alpha_{i\nu} \tau_{i\nu} s_{i\nu j} p_{i} e^{-\epsilon_{i}/kT} \frac{\epsilon_{i}}{kT^{2}} p_{j} e^{-\epsilon_{j}/kT}}{\binom{\sum\limits_{0}^{\infty} p_{i} e^{-\epsilon_{i}/kT} \binom{\sum\limits_{0}^{\infty} p_{i} e^{-\epsilon_{j}/kT}}{\binom{\sum\limits_{0}^{\infty} p_{i} e^{-\epsilon_{j}/kT} \binom{\sum\limits_{0}^{\infty} p_{i} e^{-\epsilon_{j}/kT}}}$$

$$+ \frac{1}{k_{\nu}} k_{c} T^{1/2} \frac{0}{0} \frac{\sum\limits_{0}^{\infty} \sum\limits_{0}^{\infty} \alpha_{i\nu} \tau_{i\nu} s_{ij\nu} p_{i} e^{-\epsilon_{j}/kT} p_{j} e^{-\epsilon_{j}/kT} \frac{\epsilon_{j}}{kT^{2}}}{\binom{\sum\limits_{0}^{\infty} p_{i} e^{-\epsilon_{j}/kT} \binom{\sum\limits_{0}^{\infty} p_{j} e^{-\epsilon_{j}/kT}}{\binom{\sum\limits_{0}^{\infty} p_{j} e^{-\epsilon_{j}/kT}}{\binom{\sum\limits_{0}^{\infty} p_{j} e^{-\epsilon_{j}/kT}}}$$

$$- \frac{\sum\limits_{0}^{\infty} p_{i} e^{-\epsilon_{i}/kT} \frac{\epsilon_{i}}{kT^{2}}}{\sum\limits_{0}^{\infty} p_{j} e^{-\epsilon_{j}/kT}} \frac{\sum\limits_{0}^{\infty} p_{j} e^{-\epsilon_{j}/kT}}{\sum\limits_{0}^{\infty} p_{j} e^{-\epsilon_{j}/kT}}$$

An examination of the terms in the above equation shows that it may be rewritten in the form

$$\frac{\partial \ln k_{\nu}}{\partial T} = \frac{1}{2T} + \frac{\tilde{\epsilon}_{A} + \tilde{\epsilon}_{B} - \tilde{\epsilon}_{A} - \tilde{\epsilon}_{B}}{kT^{2}}$$
(12)

where $\tilde{\epsilon}_A$ is the average energy before activation of the molecules of A which pick up radiant energy and then react, $\tilde{\epsilon}_B$ is the average energy of the molecules of B which enter into the reaction and $\tilde{\epsilon}_A$ and $\tilde{\epsilon}_B$ are the average energies of all the molecules present. If it is desired, Equation 12 can be rewritten in the form

$$\frac{\partial \ln k_{\nu}}{\partial T} = \frac{1}{2T} + \frac{\tilde{\epsilon} - \tilde{\epsilon}}{kT^2} \tag{12a}$$

where $\bar{\epsilon}$ is the average energy of the pairs of molecules of A and B that actually enter into the photochemical reaction and $\bar{\epsilon}$ is the average energy of any pair of molecules of A and B. Except for the negligible term 1/(2T) Equation 12a has the same form as Equation 7 for monomolecular reactions. It should be noted that the term 1/(2T) arises from the assumption that the number of collisions of the molecules of the gas is proportional to the square root of the absolute temperature. In the case of reactions taking place in a liquid medium, the decrease in the viscosity of the liquid with rise of temperature might be accompanied by a considerable increase in the chance of collision, so that a larger but probably roughly calculable term would have to be introduced.

Equations 12 and 12a were derived for a bimolecular reaction in which only one of the reacting substances was activated by the radiant energy in question. In case activation of both substances were involved the rate of reaction would no longer be proportional simply to the first power of the energy density and a somewhat more complicated treatment is necessary which is hardly worth considering at the present stage of experimental

knowledge. Even in the case of a polymerization such as that of anthracene, it is not probable that both anthracene molecules are activated in an appreciable fraction of the collisions which lead to reaction, while in the case of reactions between unlike molecules one of the components is very often photo-active in the region of the spectrum used and the other inactive.

No treatment will be given at the present time of reactions of higher order than the second, since higher order collisions are of very improbable occurrence, and total changes of higher order than the second probably take place in many cases as the result of a series of changes of lower order.

VII. The Quantity
$$\frac{\partial}{\partial \nu} \left(\frac{\partial \ln k_{\nu}}{\partial T} \right)$$

Before proceeding to an interpretation of experimental data let us consider the change in temperature coefficient with frequency. It is evident that the differentiation of either of the equations, 7 or 12a, for the two cases we have treated will lead to the same result, namely,

$$\frac{\partial}{\partial \nu} \left(\frac{\partial \ln k_{\nu}}{\partial T} \right) = \frac{1}{kT^{2}} \frac{\delta \tilde{\epsilon}}{\delta \nu} \tag{13}$$

VIII. Relation between Two Methods of Expressing Temperature Coefficients

Temperature coefficients for rate of reaction are unfortunately usually expressed as the ratio r between the rates of reaction at temperatures separated by an interval of 10 °C., in accordance with the expression

$$r = \frac{k_{T+10}}{k_T} \tag{14}$$

Expressing temperature coefficients in the more rational way adopted in this article, it is evident that we may write as a rough approximation

$$\frac{\partial \ln k_{\nu}}{\partial T} = \frac{k_{T+10} - k_T}{10 (k_{T+10} + k_T)/2} = \frac{r - 1}{5(r + 1)} \,, \tag{15}$$

We may now proceed to the interpretation of existing experimental data.

IX. Interpretation of Experimental Values of Temperature Coefficients

The most striking fact concerning the temperature coefficients of photochemical reaction rates is the extremely great number of reactions for which the value of r is unity or only slightly greater than unity. Plotnikow, in his admirable collection of existing information on photochemistry, lists 21 photochemical reactions for which the maximum value of r is 1.08.

The existence of such a group of reactions is readily understood on the basis of the developments presented in this article. The value unity for r means, in accordance with Equation 15, the value zero for $\partial \ln k_{\nu}/\partial T$.

⁵ Plotnikow, "Lehrbuch der Photochemie," de Gruyter and Co., Berlin and Leipzig, 1920, p. 62.

Hence, in accordance with Equation 7 for monomolecular reactions, and also in accordance with Equation 12a for bimolecular reactions, provided we neglect the small term arising from increased frequency of collision, we may write

$$\frac{\partial \ln k_{\nu}}{\partial T} = \frac{\bar{\epsilon} - \bar{\epsilon}}{kT^2} = 0 \tag{16}$$

and may conclude that for this great group of well-known photochemical reactions the average energy of the molecules which enter into the reaction is practically the same as the average energy of all the molecules. This result is entirely understandable, since it merely means that the average molecule has as good a chance of picking up energy and becoming activated as the molecules in some special quantum state far removed in energy content from the average. For reactions of this group, preliminary partial activation of the molecule is not necessary in order that the molecule may absorb its quantum and react.

The above discussion also makes it clear that we ought to expect to find cases in which preliminary activation of the molecules is advantageous in promoting reaction. This may arise either because molecules in the lower quantum states are not in a condition to absorb radiant energy of the frequency used, or because the energy level which they attain after the absorption is not high enough to lead to chemical reaction. In such cases the average energy $\bar{\epsilon}$ of the molecules which enter into the reaction will be greater than the average energy $\bar{\epsilon}$ of all the molecules and we shall find

$$\frac{\partial \ln k_{\nu}}{\partial T} = \frac{\bar{\epsilon} - \bar{\epsilon}}{kT^2} > 0$$
, and $r = \frac{k_{T+10}}{k_T} > 1$ (17)

As a matter of fact, Plotnikow⁵ lists 17 reactions in which the ratio r varies from 1.17 to 1.50. Plotnikow believes that these reactions can be divided into two sub-groups having the approximate values for the ratio r of 1.20 and 1.40, and is also inclined to believe that the value 1.20 should be ascribed to the increase with temperature in the velocity of some diffusion process involved in the reaction, so that there would be only two true photochemical temperature coefficients, corresponding to r = 1.00 and r = 1.40.

On the basis of the theoretical developments presented in this article, there seems to be no ground for the point of view of Plotnikow. The most significant term in determining the value of the temperature coefficient will be $\bar{\epsilon} - \bar{\epsilon}$ which is the difference between the average energy of the molecules which actually react and the average energy of all the molecules. This quantity will depend on the energy levels for the different quantized states of the particular substances involved and there is no reason why different substances should all have the same value of $\bar{\epsilon} - \bar{\epsilon}$. The value zero for $\bar{\epsilon} - \bar{\epsilon}$ is a very natural one to expect and this accounts

for the large group of photochemical reactions with zero temperature coefficient, but there is no reason to suppose that when $\tilde{\epsilon} - \tilde{\epsilon}$ is greater than zero it will be the same for different kinds of molecules as would be necessary to account for a unique value r=1.40.

In the case of second order reactions, in addition to the effect of the term $\bar{\epsilon} - \bar{\epsilon}$ in determining temperature coefficients, we shall also have to consider, as pointed out above, the effect of temperature in increasing the number of collisions between the reacting molecules. In gaseous systems the number of collisions will be roughly proportional to the square root of the absolute temperature and this will produce a negligible increase in reaction velocity with increasing temperature. In liquid systems the decrease in viscosity with rising temperature may be large enough to produce a measurable effect on reaction velocity. Similar considerations will apply to heterogeneous reactions where diffusion of the reacting substances to a catalytic surface is necessary for reaction. Since the viscosity of water at room temperature decreases about 20% for a 10° rise. this might account in some cases as suggested by Plotnikow for a value r = 1.20. It should be noted, however, that of the 7 reactions which Plotnikow lists as belonging to the group with the value 1.20, 3 are gaseous reactions, so that his explanation can hardly be a general one.

Further evidence as to the tenability of the theory of temperature coefficient here presented, is afforded by a calculation of the magnitude of $\bar{\epsilon} - \bar{\epsilon}$. If in accordance with Equations 7 and 15 we write

$$\frac{\partial \ln k_v}{\partial T} = \frac{\bar{\epsilon} - \bar{\epsilon}}{kT^2} = \frac{r - 1}{5(r + 1)},$$

and take r=1.40 and $T=300^\circ$, as typical, we obtain for $\bar{\epsilon}-\bar{\epsilon}$ the value 6000 cal. per mol. This corresponds to a value of 0.26 volts per molecule which is an entirely reasonable figure for the difference in energy contents between successive quantum levels in a molecule.

A monomolecular photochemical reaction taking place at room temperature in a homogeneous system with a temperature coefficient corresponding to r=1.40 might be very reasonably interpreted by assuming that the molecules in the lowest quantum state were not photo-active, and that molecules had to be in the next highest quantum state with a preliminary activation corresponding to 0.26 volts in order to absorb light and react. The relative numbers of molecules in the first and second quantum states would be given in accordance with Equation 3 by the expression

$$\frac{N_1}{N_2} = \frac{p_1 \ e^{-\epsilon_1/kT}}{p_2 \ e^{-\epsilon_2/kT}}$$

Since the ratio of the a-priori probabilities p_1/p_2 is certainly small, we may temporarily take it as unity; substituting the value of $\bar{\epsilon} - \bar{\epsilon}$ corresponding to 0.26 volts we then obtain for our particular case the ratio,

 $N_1/N_2=22,000$. We thus see that practically all the molecules will be in the lowest quantum state⁶ and that the difference, $\bar{\epsilon}-\bar{\epsilon}$, between the average energy of the molecules which react and the average energy of all the molecules will be approximately, as assumed above, the difference between the energy levels in the lowest and next to the lowest quantum states. The process of reaction itself will consist in the picking up of a quantum $h\nu$ by molecules in the next to the lowest quantum state followed by reaction. If the photo-active light has the wave length $500\mu\mu$ this denotes a further increase in energy level corresponding to an activation of 2.5 volts per molecule, again an entirely reasonable figure.

Before leaving the subject of temperature coefficients, the question naturally arises whether negative temperature coefficients might be possible, owing to the fact that molecules in the lowest quantum state could pick up radiant energy of the frequency employed and molecules in the second quantum state not be able to do this. It will be seen from the above discussion, however, that at room temperature with probable values of the difference in energy between the first and second quantum states, nearly all the molecules in any case would be in the lowest quantum state, and negative temperature coefficients would not be probable since a lowering of the temperature would not appreciably increase the percentage of molecules in the lowest quantum state.

X. Interpretation of Experimental Values of $\frac{\partial}{\partial \nu} \left(\frac{\partial \ln k_{\nu}}{\partial T} \right)$

In Section VII we showed that the change in temperature coefficient with frequency for a photochemical reaction is given by the equation

$$\frac{\partial}{\partial \nu} \left(\frac{\partial \ln k_{\nu}}{\partial T} \right) = \frac{1}{kT^2} \frac{\partial \bar{\tilde{\epsilon}}}{\partial \nu}$$

Since $\bar{\epsilon}$ is the average energy of the molecules that actually react, this quantity may decrease with frequency, for at higher frequencies the magnitude of the quantum $h\nu$ is increased and molecules from a lower quantum state may be raised to a level where reaction is possible. This means that we may expect to find cases where the second derivative in question is negative, provided $(\partial \ln k_{\nu}/\partial T)$ is not already zero.

Experimental data of the kind in question are not numerous nor certain. Nevertheless, referring once more to Plotnikow's treatise, we find that silver citrate paper has the temperature coefficient r = 1.19 in the blue and 1.07 in the ultraviolet; the phototropic substance salicylidene- β -

⁶ We exclude the possibility of an appreciable number of molecules in quantum states higher than the second owing to the still greater energy of these states, and the increased volume which would accompany the higher states. For the case of monatomic hydrogen, the distribution of atoms in the different quantum states, allowing for the increased volume of the atom in the higher quantum states, has been treated by Urey in an article which will probably appear in the Astrophysical Journal.

naphthylamine has the values 1.8 in the green, 1.45 in the blue and 1.39 in the violet; and the reaction between chlorine and hydrogen has the values 1.50 for green light (550–530 $\mu\mu$), 1.31 for blue light (490–470 $\mu\mu$) and 1.21 for violet light (400–350 $\mu\mu$). These results if reliable are in complete agreement with the theory here presented.

XI. Remarks on Einstein's Law of Photochemical Equivalence

Although the main purpose of this article has been to consider the temperature coefficient of photochemical rate of reaction, a few words concerning Einstein's law of photochemical equivalence will not be out of place. According to this law the number of molecules that enter into a photochemical reaction should be equal to the number of quanta of radiant energy absorbed. It is evident from the discussion presented in this paper, however, that molecules may sometimes absorb a quantum of energy and then lose it by re-emission before reacting. This would be true in the case of monomolecular reactions unless the quantity sin occurring in Equation 6 should be unity, and in the case of bimolecular reactions unless the product $\tau_{i\nu}$ $s_{i\nu}$, occurring in Equation 11 should be great enough to assure reaction for every molecule activated. Thus we should expect to find many reactions in which the actual amount of reaction falls below that predicted by an over simplified statement of Einstein's law, and this agrees with the experimental facts.7 Cases might also occur in which the primary photochemical reaction is followed by secondary reactions which would make the total change greater than that predicted. case apparently occurs under certain conditions in the reaction between hydrogen and chlorine and has been discussed by Nernst.⁸ The situation may be summed up by stating that although Einstein's law of photochemical equivalence presumably holds for individual molecular changes it may not hold for the total end result of a photochemical reaction as macroscopically determined.

XII. Conclusion and Summary

- 1. A simple equation for the temperature coefficient of photochemical reaction rate has been derived on the basis of the quantum theory. The equation agrees with that previously obtained by the author using the methods of the classical statistical mechanics.
- 2. Existing data on temperature coefficients of photochemical reactions have been successfully interpreted with the help of the equation. It has been shown that Plotnikow's division of photochemical temperature coefficients into three distinct classes is apparently not tenable.
- ⁷ For the best work in this field see Warburg's papers in the Berichte der Berliner Akadamie.
 - 8 Nernst, Z. Elektrochem., 24, 335 (1918).

- 3. An equation for change in temperature coefficient with frequency has been derived and successfully used in interpreting existing data.
- 4. The causes for apparent deviations from Einstein's law of photochemical equivalence have been discussed.
- 5. Experimental work in this Laboratory is now in progress for further testing the ideas presented in this article.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE ADSORPTION OF GASES BY COPPER

By Robert N. Pease¹ Received July 11, 1923

During a recent investigation of the combination of ethylene and hydrogen in the presence of metallic copper,² a considerable amount of data on the adsorption isotherms of hydrogen, ethylene, ethane and carbon monoxide on copper was accumulated. As these results show many points of special interest, it has seemed worth while to devote a separate paper to them.

The apparatus, procedure and method of preparation of the copper and the gases have already been described² and need not be repeated here in detail. Suffice it to say that adsorptions at a series of pressures between 0 and 760 mm. were determined by admitting the gases in small quantities to an evacuated bulb containing the copper and measuring the pressure after equilibrium had been established. The dead space in the bulb and connecting tubes was determined by the use of helium, which was assumed not to be adsorbed.

The absorbent consisted of about 100 g. of copper granules prepared by reduction of copper oxide by hydrogen at 200° in its original position.

Adsorption Isotherms on Active Copper at 0°

The adsorption isotherms at 0° in the presence of active copper are shown graphically in Fig. 1. Ethane was not actually run on this sample but its comparative behavior is known from two other series on similar samples of copper. An isotherm has been sketched in for completeness. Nitrogen was also run on this sample but the variability of the results indicated the presence of varying but small quantities (less than 0.5%) of some strongly adsorbed impurity. The nitrogen was prepared from ammonium chloride and sodium nitrite and was purified by passage through sulfuric acid, phosphorus pentoxide and a tube cooled in a mixture of solid carbon dioxide

¹ The work represented by this paper was performed while the author was National Research Fellow at Princeton University.

² Pease, This Journal, 45, 1196 (1923).

and alcohol. A curve corresponding to the least adsorption noted for nitrogen has been sketched in. From the form of this particular curve, it would appear that this particular sample of nitrogen contained negligible amounts of impurity.

The marked specificity of the adsorption is conclusively demonstrated by the results of these measurements; for the order of adsorption not only bears no simple relation to the order of boiling points (that is, condensa-

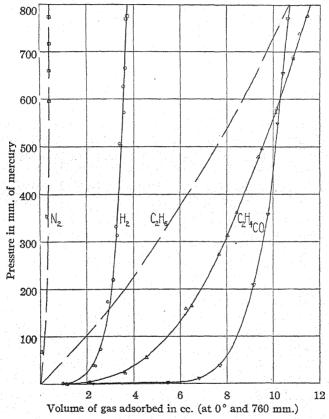


Fig. 1.—Adsorptions of N₂, H₂, C₂H₆, C₂H₄ and CO on active copper at 0°. Weight of copper catalyst: 117.0 g. Volume of dead space: 58.50 cc.

bility) but in addition depends upon the pressure at which comparison is made. Thus, at 10 mm. pressure the order of adsorptions is N₂, C₂H₆, H₂, C₂H₄, CO; while at 760 mm., the order is N₂, H₂, C₂H₆, CO, C₂H₄; and from the slopes of the curves it is evident that at still higher pressures the order will be N₂, H₂, CO, C₂H₄, C₂H₆. The order of boiling points is H₂, N₂, CO, C₂H₄, C₂H₆. The marked difference in the behavior of nitrogen and carbon monoxide toward copper is especially to be emphasized in view of the similarity in many physical properties of these two gases.

Leaving nitrogen out of account for the moment, certain interesting relationships among the adsorptions are clear. It is plain that the curves for hydrogen, carbon monoxide and ethylene are similar in form.3 There is a portion representing adsorption at a pressure of less than 0.2 mm. which amounts to about 1 cc. for hydrogen, 2 cc. for ethylene and 4 cc. for carbon monoxide, a second portion pronouncedly concave to the pressure axis and a third portion which is nearly rectilinear. The curve for ethane differs from the above in showing no marked low-pressure adsorption and being slightly concave to the pressure axis over the whole range. It is of interest that the slopes of the curves at 1 atm. for the four gases stand in the order of boiling points, that of hydrogen (expressed in cc. per 10 mm.) being 0.010, of carbon monoxide 0.020, of ethylene 0.065 and of ethane 0.092. If it were not for the fact that the slope of the nitrogen curve is certainly much less than that of hydrogen, one might be inclined to say that the adsorption at the higher pressures was due to the "physical" forces of capillarity. There would still be the difficulty that this implied the liquefaction of the gases in the capillaries of the copper at temperatures which for hydrogen and carbon monoxide are much higher than the critical, though not for ethylene and ethane ($t_c = 9.5^{\circ}$ and 32.1°, respectively).

Much time was spent in attempting to fit the data to various adsorption equations to be found in the literature, but it was found that none reproduced satisfactorily the values for the concave portions of the curves, that is the adsorptions up to about 0.5 atm. The best fit was obtained with a modification of Langmuir's equation for adsorption on a single type of elementary space. The simple equation may be written, $V_{\rm ads.} = [ap/(1+ap)]V_{\rm sat.}$, in which a and $V_{\rm sat.}$ are constants.

According to this equation, when ap is large compared to unity, $V_{\rm ads.} = V_{\rm sat.} = a$ constant, and when ap is small compared to unity, $V_{\rm ads.} = ap$ $V_{\rm sat.} = {\rm const.} \times p$. The coefficient, a, may be taken as a measure of the strength of the adsorption. It is probable that with an adsorbent such as the copper granules used in the work, elementary spaces or active adsorbing centers of all degrees of activity are scattered over the surface and that before Langmuir's equation can be properly applied, the "distribution curve" for activity must be known.⁴ We may assume, however, that over the range of pressure considered these activities may be grouped around three average values corresponding to (1) a high activity and large value of a (for which $V_{\rm ads.} = V_{\rm sat.}$); (2) a medium activity and medium value of a (for which $V_{\rm ads.} = [ap/(1+ap)]V_{\rm sat.}$) and a low activity and low value of a (for which $V_{\rm ads.} = [ap/(1+ap)]V_{\rm sat.}$). We may then write $V_{\rm ads.} = apV_{\rm sat.}$).

Adsorption curves for CO on copper like those here reported had been previously obtained by H. A. Jones and H. S. Taylor in the Laboratory of Princeton University.
 Langmuir, This Journal, 40, 1361 (1918).

 $V_1+V_2+V_3=V_{\rm lsat.}+\frac{a_2p}{1+a_2p}\,V_{\rm 2sat.}+a_3V_{\rm 3sat.}\,p.$ This equation can be made to fit the experimental values for hydrogen, carbon monoxide and ethylene within the experimental error. Considering that it is a four-constant equation, which may be written $V_{\rm ads.}=A+\frac{Bp}{1+Bp}\cdot C+Dp$, this is not strange. As it may be considered to have some theoretical basis, this equation has been preferred to others, however. It may be noted that the three terms correspond in a way to the three portions of the characteristic adsorption isotherms. The best values of the four constants for hydrogen, carbon monoxide and ethylene are given in Table I.

Table I
Values of Constants in Adsorption Equation

:	$V_{1sat.}$	$V_{2sat.}$	a_2	as V sant.
H_2	0.95	2.21	0.037	0.000855
C_2H_4	1.95	4.34	.0173	.00658
CO	4.95	4.74	.0419	.00191

The Effect of Poisoning the Copper with Mercury

Since previous experiments had demonstrated that mercury was a very powerful catalyst poison in the ethylene-hydrogen combination and that adsorption runs approximately parallel to catalytic activity, it was of interest to investigate further the influence of poisoning on the latter property. Accordingly, with the sample of copper used in the experiments just described, the influence of mercury on the adsorptions of hydrogen, ethylene and carbon monoxide at 0.° was determined.

A small quantity of mercury, estimated at 0.015 cc., was forced into the adsorption bulb with hydrogen, after which the bulb was evacuated and heated to 200°. During the heating a few small globules of mercury condensed out on the cool portions of the connecting tube but the bulk of the mercury remained in the bulb. After heating, the mercury was found to have completely disappeared and there was no visual evidence of a change in the copper. Adsorption measurements revealed a marked decrease in activity, however.

The character of the effect of mercury poisoning is made clear by an examination of the curves in Fig. 2. (Broken curves, before poisoning; solid curves, after poisoning). It will be noted that the curves have been moved nearly parallel to themselves toward the pressure axis, corresponding to decreases of different magnitudes mainly in the strong (low pressure) adsorption. The amounts of these decreases in adsorption at 1 atmosphere are 4.85 for carbon monoxide, 3.40 for hydrogen and 1.60 for ethylene; at 100 mm. the decreases are 5.00, 2.70 and 1.90, respectively.

It is not clear why these decreases should vary so much among themselves, if the effect of mercury is to saturate permanently a certain number of elementary spaces. In particular, the result seems to be at odds with a conclusion arrived at in another paper.² There it was shown that when a mixture of ethylene and hydrogen was let into the bulb containing copper catalyst, the initial pressure (obtained by extrapolation) was what would be expected if the total amount of gas adsorbed were equal to the amount of ethylene alone which would have been adsorbed if it alone were present. This did not necessarily mean that no hydrogen was adsorbed under these conditions. In fact, quite the opposite was indicated by the results of

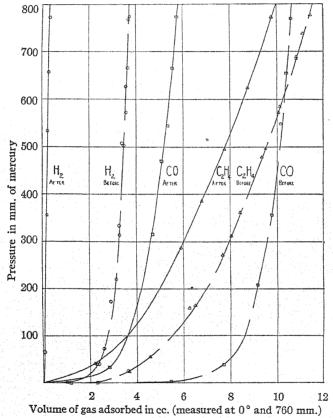


Fig. 2.—Adsorptions of H₂, C₂H₄ and CO on copper before and after poisoning with mercury. Broken curves: before poisoning. Solid curves: after poisoning. Weight of copper catalyst: 117.0 g. Volume of dead space: 58.50 cc.

the research as a whole. Rather the result was interpreted to mean that those active centers on the catalyst surface which could hold hydrogen molecules were also among those which could hold ethylene molecules, so that any hydrogen adsorbed from a mixture of the two simply displaced an equivalent amount of ethylene from the surface, one molecule of hydrogen replacing one of ethylene. The writer would have been inclined

to predict from this that the mercury would have decreased the adsorptions of the two gases by like amounts, whereas it actually decreases that of hydrogen about twice as much as that of ethylene. It would seem that de-activation of the active centers could proceed in steps, so that while a given active center was completely prevented from adsorbing molecules of hydrogen, it could still adsorb ethylene strongly. Carbon monoxide, which is the most strongly adsorbed of the three, is also most affected by the mercury, its adsorption being decreased about three times as much as that of ethylene. The fact that the decrease for ethylene is both absolutely and relatively the least of the three may be connected with its relative ease of condensation.

It may be mentioned that the decreases in adsorptive capacity were accompanied by a decrease in catalytic activity toward ethylene-hydrogen combination in the ratio of more than 200:1. It is only at very low pressures that the decreases in adsorption approach this ratio. This would seem to be conclusive evidence that the strongest adsorbing centers are responsible for the main part of the catalytic activity of the preparation.

Effect of De-activation by Heat Treatment

In the course of the experiments on the catalytic combination of ethylene and hydrogen, the effect on both catalytic activity and adsorptive capacity of partially de-activating a copper catalyst by heating it to 450° in a vacuum was determined.⁵ As this gave results which differ somewhat from those obtained by de-activation with mercury, they are also included.

The results of measurements of adsorption of ethylene and hydrogen before and after heating the copper adsorbent to 450° are shown graphically in Fig. 3. It will be seen that the effect of de-activating this sample of copper by heating was in a general way similar to the effect of de-activating the other sample by poisoning it with mercury. The curves have been moved over toward the pressure axis to nearly parallel positions, at the higher pressures at least. The heating has, however, decreased the hy-

⁵ Interesting results on the effects of heating active copper to successively higher temperatures have been obtained in the course of this investigation. In the present instance, the catalyst had been prepared at 200°, and heated to 300° after reduction. It had not thereafter been taken above 200°. After the experiments on the active material so obtained had been carried out, the catalyst was heated first to 350° for an hour and then to 400° for ¹/₂ hour without a marked change in activity resulting. It was then heated to 450° for one hour after which it was found to have decreased in activity as will be shown. Further heating at 450° for ¹/₂ hour was without noticeable effect, however. Similar results were obtained with another catalyst which was eventually heated to 550° to produce a very inactive material. For each rise in temperature a noticeable decrease in activity occurred but further heating at the same temperature was without marked effect. There seems, therefore, to be a stable condition of the surface corresponding to the highest temperature to which it has been heated. All the heatings described above were carried out in a vacuum.

drogen adsorption relatively less than the poisoning and the ethylene adsorption relatively more. Thus, at one atmosphere the decrease in hydrogen adsorption amounts to 70%, while the decrease in ethylene adsorption amounts to 22%. These are to be compared with decreases of

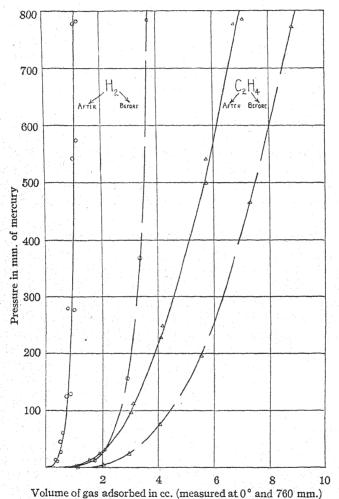


Fig. 3.—Adsorptions of H_2 and C_2H_4 on copper at 0° before and after de-activation by heating to 450° in a vacuum. Broken curves: before heating. Solid curves: after heating. Weight of copper catalyst: 94.9 g. Volume of dead space: 47.05 cc.

92% for hydrogen and 14% for ethylene caused by mercury poisoning. The absolute decreases at one atmosphere are 2.60 for hydrogen and 1.95 for ethylene. It will be seen that these figures are much more nearly of the same order than in the case of copper poisoned with mercury.

The decrease in catalytic activity in the ethylene-hydrogen combination accompanying these decreases in adsorption amounted to 85%. Just as in the case of the poisoning by mercury, one must go to very low pressures to find a corresponding decrease in adsorption, indicating again that it is the strong (low-pressure) adsorption which is mainly responsible for catalytic activity.

Seat of the Adsorptive Action of Active Copper

It is clear from the relative adsorptions of the different gases by active copper that we may at once conclude that ordinary condensation in capillaries is not a sufficient explanation of the results, although it may account for the adsorption of ethane and partially for that of ethylene. The action seems rather to be a specific one between the copper surface and the particular gas. It seems probable, however, that any copper surface will not do but that the surface must be in a special condition. 6 From the evidence here presented, taken in conjunction with previous experience in the Princeton Laboratories, it would seem that an active copper surface is one which has scattered over it regions containing atoms whose fields are highly unsaturated. This follows from the fact that heating active copper to temperatures as low as 450° caused appreciable sintering besides decreasing the surface activity. Sintering at so low temperatures points to the pre-existence on the surface of atoms of high mobility and therefore in a state of unsaturation. The process of sintering is the process of saturation of these atoms and since the agency which causes the sintering also decreases the surface activity, it is reasonable to look upon these unsaturated atoms as the cause of this activity. One would look for atoms of this character in surfaces of high degree of curvature—in "peaks," that is to say, on the copper surface—rather than in the "valleys," or capillaries.

It seems probable that each of these "peaks" can attach more than one molecule of adsorbed gas. Otherwise it is difficult to see how combination of ethylene and hydrogen, for example, can take place as a result of adsorption. As already pointed out, since each hydrogen molecule that is adsorbed apparently displaces an ethylene molecule, the same point on the copper surface cannot hold a molecule of both. The two must, however, be in close juxtaposition if combination is to occur. This can be true only if a given peak possesses more than one possible point of attachment. The activity is, therefore, not due to isolated active atoms scattered over the surface but to groups of these atoms.

It has sometimes been assumed that catalysts owe their activity to the presence of an allotropic form. While this cannot be rated very highly as an explanation, still it appeared to be of interest to find whether active

⁶ See Taylor and Burns [This Journal, 43, 1273 (1921)], Gauger and Taylor [ibid., 45, 920 (1923)] and Benton, [ibid., 45, 887, 900 (1923)] on the effect of method of preparation and of heat treatment on adsorptive capacity.

copper had the same crystalline structure as inactive. Accordingly, at the suggestion of Dr. A. W. Hull, the General Electric Research Laboratory was requested to make an X-ray analysis of a sample of active copper and very kindly consented to do so. The analysis proved that active copper has the same arrangement and spacing of atoms as ordinary massive copper, thus disposing of the assumption of a different allotropic form. This result also indicates that amorphous metal does not exist in any quantity on the surface. The discovery by Scheerer that metals preserve their characteristic crystalline arrangement and spacing of atoms even when in the colloidal state would render the existence of amorphous copper in the material used still more doubtful.

The peculiar appearance of active copper (it usually has a dull, reddish-brown surface) may be laid to its fine state of subdivision rather than to the presence of another form. Platinum black and precipitated silver behave similarly. Wood⁹ has suggested that the phenomenon is probably due to the "trapping" of the incident light in the pores of the substance by multiple reflection and consequent abnormally large adsorption.¹⁰

Apparent Density of the Copper Adsorbent

As a check on the determination of the dead space with helium on one sample of copper, determinations were also carried out by filling the exhausted bulb with water after the experiments were concluded. The value obtained with helium was 47.05 and with water was 47.13 after correction had been made for the volumes of the connecting tubes. The volume of the empty bulb was also determined and was found to be 58.00 cc., after applying the above correction. From these data the apparent density of the copper can be calculated. The average of the two values for the dead space, 47.09 cc., will be used.

	Vol. cc.	
Empty bulb		Wt. of copper = 94.925 g.
Dead space	47.09	wt. 94.93
Copper	10.91	Dens. of copper = $\frac{\text{wt.}}{\text{vol.}} = \frac{94.93}{10.91} = 8.70$
		Dens. of massive copper ¹¹ = 8.935

⁷ This request was made by Dr. Arthur F. Benton who prepared the sample and sent it in for investigation.

⁸ Scheerer, Appendix to Zsigmondy's "Kolloidchemie," 4th Edition, 1922, p. 387.

⁹ Wood, "Physical Optics," Macmillan Co., 1921, p. 449.

¹⁰ A sample of active copper recently prepared in the writer's laboratory has the characteristic appearance of ordinary copper and yet possesses high activity both as a catalyst and as an adsorbent with this exception, namely, that the adsorption of ethylene is almost the same as that of hydrogen instead of being two or three times as great. Accepting Wood's explanation, the appearance of this sample indicates that it is non-porous. The absence of large adsorption of ethylene at higher pressures is a strong indication that such adsorption is due to capillary condensation.

¹¹ Landolt-Börnstein "Tabellen," Julius Springer, 1905, p. 226.

The active copper is seen to have an apparent density lower by about 2.5% than that of massive copper. Since the X-ray analysis of a sample of active copper just mentioned showed that the copper had the normal arrangement and spacing of atoms, it is evident that the low density is probably due to the presence of cavities within the mass into which neither helium nor water penetrated.

Summary

- 1. The adsorption isotherms of hydrogen, ethylene, ethane, carbon-monoxide and nitrogen at 0° and up to one atmosphere have been measured. The results are discussed and the specific nature of the adsorption emphasized.
- 2. The effect of poisoning the copper with mercury on the adsorptions of hydrogen, ethylene and carbon monoxide and the effect of partially deactivating copper by heating on the adsorptions of hydrogen and ethylene have been determined. In both cases it has been found that the strong adsorption at low pressures has been markedly decreased while the additional adsorption at higher pressures has suffered little or not at all.
- 3. From these results and certain incidental observations it has been concluded that the adsorption is due to specific adsorbing centers on the copper surface rather than to the surface as a whole. These centers, it seems most reasonable to suppose, are regions of high curvature or "peaks" on the surface.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC OXIDATION OF CARBON MONOXIDE. I. EFFICIENCY OF THE CATALYSTS, MANGANESE DIOXIDE, CUPRIC OXIDE AND MIXTURES OF THESE OXIDES

By J. A. Almquist and William C. Bray Received July 18, 1923

In connection with the work of the Defense Research Section, C. W. S., it was discovered 1,2,3,4 that specially prepared mixtures of certain oxides catalyzed the combustion of carbon monoxide at low concentration in air. The catalyst composed of 60% of manganese dioxide and 40% of copper oxide furnished a striking example of the "mixture effect" in contact ca-

- ¹ Lamb, Bray and Frazer, J. Ind. Eng. Chem., 12, 213 (1920).
- ² Rogers, Piggott, Bahlke and Jennings, This Journal, 43, 1973 (1921).
- ³ Merrill and Scalione, ibid., 43, 1982 (1921).
- 4 Lamb, Scalione and Edgar, ibid., 44, 738 (1922).
- ⁵ The mixture effect is probably closely related to promoter action. For a discussion of a number of examples, see Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

talysis, since with dry gas it had been made to operate at high efficiency at a temperature as low as 0°, although each of its components was active only at a much higher temperature.

In 1920, an investigation of the mixture effect was begun in this Laboratory, and the manganese dioxide-copper oxide catalysts for the combustion of carbon monoxide were chosen for study. It was planned to obtain as complete data as possible for several series of catalysts, varying in composition from pure manganese dioxide to pure copper oxide, rather than to attempt to prepare especially active catalysts. In order that the results for each series might give comparable data on the mixture effect, all of the catalysts of one series were prepared from the same moist samples of the individual oxides, and were dried under similar conditions. The program included the study of catalytic activity, adsorption and desorption of the gases involved, and the pore volume of the catalysts.

Since the completion of our work the results of a related investigation by Benton⁶ have been published, in which special attention was paid to the adsorption of gases by several oxide catalysts, including manganese dioxide, cupric oxide, and one mixture of these oxides. The experimental details differ greatly in these two independent investigations, and each will be a useful supplement to the other.

The present paper deals primarily with the activity of the catalysts. A satisfactory measure of activity, as has been pointed out in earlier papers^{2,4}, is the efficiency of the catalyst at a given temperature, or is the temperature corresponding to a given efficiency, when a "steady state" has been attained. It was found that a definite efficiency could be obtained for each catalyst provided that certain experimental conditions, as the temperature and volume of the catalyst, the rate of flow of the gas, and the partial pressure of water vapor, were kept constant. The results of the measurements, under controlled conditions, and in general with dry gas, are given in the form of efficiency-temperature curves, the efficiency being expressed as the percentage of the carbon monoxide oxidized in passing through the catalyst. The curves do not intersect, and their positions with reference to the temperature axis give a convenient measure of the relative activities of the catalysts.

In general, a very low concentration of carbon monoxide in air, approximately 0.2%, was used in these tests. Higher concentrations would have introduced a complication due to the greater heat of combustion in the mass of the catalyst. However, the precaution of measuring the temperature within the catalyst, when operating under constant conditions, prevented any error due to this heating effect. In fact, it was proved for one catalyst that the same efficiency-temperature curve was obtained when the carbon monoxide concentration was varied between 0.1% and 0.6%.

⁶ Benton, This Journal, 45, 887, 900 (1923).

Preparation of the Catalysts

The manganese dioxide and copper oxide were prepared according to the directions of Merrill and Scalione⁷ except that larger quantities were used. However, we believe that products of this type made by different investigators or at different times may vary greatly in properties.

In the preparation of the *basic copper carbonate*, the directions of Merrill and Scalione⁸ were followed except that it was not precipitated on the manganese dioxide. The product was a fine, green precipitate and settled rapidly.

Three series of catalysts were prepared. Each consisted of six members, the pure components, and four mixtures of the following approximate compositions: 80% MnO₂, 20% CuO; 60% MnO₂, 40% CuO; 40% MnO₂, 60% CuO; 20% MnO₂, 80% CuO. The catalysts of each series will be referred to later by numbers from 1 to 6, in the order of decreasing manganese dioxide content.

In each series the moist constituents were mixed in the desired proportions, drained on a filter, and the six samples in the form of filter cakes dried slowly at about 75° for 72 hours in an electric oven. In each case the resulting material was broken up, and granules which passed a 10-mesh screen and were retained on a 20-mesh screen were collected and stored in well-stoppered bottles. Before these granules were tested or analyzed, they were given a final drying for half an hour at 175° under a pressure of about 1/3 atmosphere.

The catalysts of Series 1 were later found to contain soluble sulfates, and in some cases seemed not to have been well mixed. Accordingly, in the two later series the constituents were washed more carefully during their preparation, and the mixing was done by grinding the moist oxides in a large mortar until a uniform paste resulted. The basic copper carbonate (No 6, Series 3) had a tendency to pulverize on drying and did not give satisfactory granules. No. 5 in the same series gave very soft granules.

Three catalysts prepared by the Washington investigators were also tested: manganese dioxide, a 60% (MnO₂) mixture, and copper oxide. Portions of the original samples were given the usual half-hour heat treatment under diminished pressure at 175° before being tested. These catalysts are numbered W1, W3, and W6 respectively, but do not constitute a related series. The methods of preparation of the two oxides, W1 and W6, were similar to those used by us; but the mixture, W3, is not directly comparable with any of our mixtures. It is probably closely related to or identical with that used by Lamb, Scalione and Edgar. Its properties, which will be presented later, indicate that its constituents differed from those of the other mixtures, but may be partly accounted for by the pressure treatment to which the moist filter cake was subjected.

⁷ Ref. 3, p. 1986.

⁸ Ref. 3, p. 1987.

⁹ Ref. 4, p. 740, Footnote 6.

Apparatus and Experimental Method

The general method of testing consisted in passing a mixture of carbon monoxide and air of known composition through the catalysts at a definite constant rate and determining the percentage of the carbon monoxide oxidized by analyzing the effluent gas. Since it was desirable to make analyses continuously, use was made of a calorimetric device developed by Lamb and Larson, with a modification essentially like that described by Larson and White¹¹ for the prevention of premature combustion on the thermocouple leads.

The flowmeter, A, gave a head of 35.8 cm. of water for a rate of flow of $^{5}/_{12}$ liters per minute. This corresponds to the space velocity of 5000 for 5 cc. of catalyst which was used in these tests.

E is a bead tower through which concd. sulfuric acid dripped and G is a tower containing solid sodium hydroxide for removing acid spray.

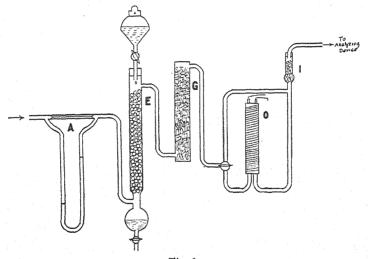


Fig. 1

The catalyst to be tested was placed in a tube at O. The testing tube was of 1 cm. cross section and the catalyst was placed therein on a perforated plate, to a depth of 5 cm. The gas passed up inside of the outer jacket and down through the catalyst contained in the inner tube. For tests above room temperature, heating was accomplished by a coil of resistance wire wound on asbestos paper around the outer tube, and the temperature was controlled by means of a lamp bank and a rheostat. The temperature within the catalyst and that just above it was measured by means of two copper-constantan thermocouples. Readings were made on a commercial potentiometer indicator to within 1° . When the catalyst was operating at 100% efficiency with 0.2% carbon monoxide air mixture, its temperature was 4° or 5° higher than that of the entering gas; but at 20% or lower efficiency the difference was not measurable. For tests below room

¹⁰ Lamb and Larson, This Journal, 41, 1908 (1919); compare Figs. 3 and 4, p. 1914.

¹¹ Larson and White, ibid., 44, 20 (1922).

temperature the entering gas was precooled before reaching the catalyst by passing through a copper tube, closely wound around the glass jacket. The apparatus was immersed in a Dewar tube containing a suitable cooling mixture and the temperature of the catalyst was measured as before.

In Fig. 1, I represents a calcium chloride drying tube, placed beyond the catalyst, which was used in all our work. It is probable that the drying of the gas at this point was unnecessary, since there is no evidence that water vapor interferes with the performance of the analyzing device.

The mixture of carbon monoxide and air used for testing was kept in a 500-liter gasometer, built of tin-plated copper and equipped with an electric fan for stirring. The carbon monoxide was prepared by the action of concd. sulfuric acid on sodium formate.

Analytical Methods

Carbon Monoxide.—The iodine pentoxide method for the determination of carbon monoxide was employed to determine the composition of the gas used for testing. The procedure followed was essentially the same as that developed by Larson, Jayson and White, Defense Research Section, C. W. S.¹² When small corrections were made by means of blanks, an accuracy of 1 to 2% was obtained for samples containing about 0.2% of carbon monoxide.

The composition of the catalysts, as determined by the following analytical methods, is shown in Tables I–IV, which are placed in the following section near the efficiency-temperature diagrams, Figs. 2–6.

Water and Carbon Dioxide in the Catalysts.—A current of air, previously dried by passing over solid potassium hydroxide and phosphoric anhydride, was aspirated slowly through a Pyrex tube containing a weighed sample of the catalyst, and then through weighed U-tubes containing phosphorus pentoxide and potassium hydroxide. The tube containing the catalyst was heated almost to redness and allowed to cool in position. The amounts of water and carbon dioxide were determined by weighing the absorption U-tubes. It is interesting to note that even the manganese dioxide (before its use as a catalyst) contained some carbon dioxide although no carbonate was used in its preparation. The only explanation is that it was absorbed from the air.

In Tables I–IV the results of these analyses are expressed as the number of grams of water or carbon monoxide per 100 g. of the water-free sample. The calculations were made by subtracting the weight of water found from the weight of the original sample. In Series 1 (Table I) the carbon dioxide content was very small and was neglected.

Available Oxygen.—The oxidizing power of the catalysts was determined by their ability to liberate iodine from a solution of potassium iodide, which was slightly acid with sulfuric acid. The oxidizing power thus determined includes the reduction of the manganese dioxide to manganese oxide and of the cupric to cuprous oxide. The liberation of iodine was

¹² Compare Teague, J. Ind. Eng. Chem., 12, 964 (1920).

slow, especially with copper present, and was not complete in some cases in less than two or three days. To prevent the oxidation of the iodide by the air during this period the solutions were kept in glass-stoppered flasks from which air had been displaced by carbon dioxide. The iodine set free was titrated with $0.1\ N$ sodium thiosulfate solution. After titration the solution was allowed to stand for 24 hours and if no color developed, the reaction was regarded as complete.

In Tables I–IV the available oxygen is shown in the fifth column as the number of grams of oxygen per 100 g. of the anhydrous sample (that is, the original material minus the water content).

An attempt was made to check the method described above by comparison with a gravimetric one. A sample of the oxide was treated as described under the determination of water, and the catalyst was weighed after the heating. The weight lost by the oxide minus the weight of water and carbon dioxide was taken as the amount of oxygen lost on heating. The available oxygen content of the same oxide before and after heating was determined by the potassium iodide method and the difference between these should also be equal to the oxygen lost. In almost every case, the oxygen loss as determined by the latter method was slightly greater than that found by the direct weighing. The discrepancy was mainly due to the fact that the oxide after being heated was extremely hygroscopic and gained some weight before it could be weighed. It was found that a momentary exposure to the air produced an appreciable increase in weight, and that the discrepancy became less as precautions to prevent exposure were increased. It was concluded, therefore, that the iodide method was the better and could be relied upon to give satisfactory results on the relative available oxygen contents of the catalysts used.

Copper Oxide.—The mixed catalyst was treated with dil. sulfuric acid and solid sodium sulfite, in excess of that required for the reduction of the manganese dioxide, was added. The oxides dissolved rapidly and the solution was evaporated until fumes of sulfuric acid appeared, in order to expel the excess of sulfur dioxide. The acid concentration was reduced to about $0.2\,N$ by addition of water, and excess of potassium iodide was added. The liberated iodine was treated with $0.1\,N$ sodium thiosulfate solution in the usual manner.

In Tables I–IV the results of these copper determinations are shown in the third from the last column as percentage of cupric oxide in the anhydrous sample.

Manganese Oxides.—After correction had been made for the water content, 100 g. of the anhydrous sample contained known amounts of carbon dioxide and cupric oxide and the remainder was assumed to be manganese oxides, MnO_x , (except in Series I, where the impurities were not negligible); x was calculated from the available oxygen content, after the

amount corresponding to the cupric oxide present had been subtracted. The values of x, given in the last column of the Tables, are always less than 2, and are not constant within a single series. While they are evidently not very accurate, they serve to show approximately the state of oxidation of the manganese oxide. Another method of representing the composition of MnO_x is shown in the tables, namely, as a mixture of manganese dioxide and monoxide; the fourth from the last column shows the amount of dioxide corresponding to the available oxygen in MnO_x , and the remainder is given in the next to the last.

The presence of impurities in the catalysts of Series 1 interfered with the determination of the MnO_x content and of x. The impurity was 4.5% in the copper oxide; and it was probably as large in the manganese oxide, No. 1, as was shown by its behavior towards water (in experiments by Draper which will be described in a later article). The value of x for this sample (No. 1) is 1.65 when the impurity is assumed to be zero, and 1.69 for 4.5% impurity. The latter value was arbitrarily assumed, and the 4.5% correction for impurities was made on all the members of Series 1.

The composition of the catalysts with respect to MnO_x and cupric oxide is shown in the second and third columns of Tables I–IV.

Results of Standard Efficiency Tests with Dry Gas

In making a run, air was passed through the line until the galvanometer deflection remained constant at or near the zero point. This indicated that the two thermocouple junctions in the analyzing device were in temperature equilibrium. The dilute mixture of carbon monoxide and air was then drawn through at a rate of 5/12 liters per minute directly to the analyzer and a constant deflection was obtained in a few minutes. By changing the resistance in the galvanometer circuit this constant deflection was made to occur at a position between 20 and 25 cm. on the scale. The gas was then turned through the catalyst tube by means of a stopcock; the reading then varied between the above maximum and zero, depending on the efficiency of the catalyst. For this analyzing device Lamb and Larson found that the calibration curve, relating deflections to carbon monoxide concentrations, was a straight line up to 0.4% of carbon monoxide. From this it follows that at these low concentrations the percentage decrease in the deflection is equal to the percentage of carbon monoxide oxidized in the catalyst tube. This gives the efficiency of the catalyst under the given conditions directly, provided that sufficient time has been allowed for a steady state to be realized.

In a given run, after the steady state had once been attained, giving one point on the efficiency-temperature curve, the determination of the other points could be made comparatively rapidly. When the temperature of the catalyst was then maintained constant for half an hour the efficiency

remained constant for the last 15 minutes of this period. However, on starting a run, either with a fresh catalyst or with a sample which had been tested on the previous day, there was some delay in attaining the steady state, and the efficiency gradually increased at constant temperature. This was especially marked when the catalyst was operating at low efficiency. Accordingly, the most satisfactory procedure was first to operate at or above the temperature corresponding to 90–100% efficiency. Each of the points marked on Figs. 3, 4 and 5 was obtained at constant temperature and the efficiency remained constant for 10 minutes. The points were shown to be reproducible whether the catalyst had previously been operating at higher or lower efficiencies.

In making the tests on Series 1 the less satisfactory method was adopted of beginning the measurements at the lower temperature, and taking a large number of readings without definitely proving that the efficiency remained constant at a given temperature. The smooth curves drawn

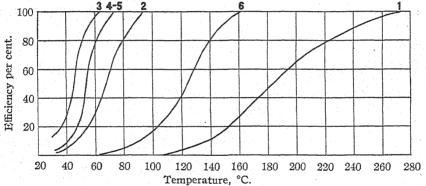


Fig. 2.—Efficiency data for Series I; compare Table I

through these points are shown in Fig. 2, but it is possible that the efficiency may be slightly low in some cases. However, when a second run was made with Catalyst 3 by the regular method, the steady-state points fell on or very close to the curve previously obtained.

The results in Fig. 2 show that the four mixtures were 100% efficient at temperatures below 90°, while the copper oxide, No. 6, and the manganese

Table I

Composition of Catalysts, Series 1. Compare Fig. 2

Composition referred to 100 g. of anhydrous sample

		Con	position referred	1 10 100 g. 0	n annyt	irous sampie	
No.	MnO_x	CuO H	Available 2O oxygen	MnO ₂	CuO	Remainder MnO + salts	æ
1	100	0 7	.5 12.8	70.0	0.0	30.0	(1.69)
2	70	30 6	.4 12.6	53.0	28.8	18.2	1.75
3	55	45 7	.5 12.2	43.0	43.2	13.8	1.78
4	42	58 7	.0 11.1	29.8	56.0	14.2	1.70
5	21	79 4	.1 10.5	15.9	75.7	8.4	1.75
6	0	100 3	.5 9.6	0.0	96.0	4.0	
				A 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			

TABLE II

Composition	OF	CATALYSTS,	Series	2.	Compare Fig. 3

			Comp	osition refer	rred to	100 g. of			
No.	MnO_x	CuO	$_{\mathrm{H_2O}}$	Available oxygen	CO_2	MnO2	CuO 1	Remainde MnO	r x
1	100.0	0.0	4.0	15.7	0.9	85.0	0.0	14.1	1.83
2	71.8	28.2	4.0	14.8	.7	65.2	28.0	6.1	1.89
3	54.9	45.1	3.7	13.1	.7	46.8	44.8	7.7	1.82
4	38.1	61.9	4.4	12.6	.7	34.8	61.5	3.0	1.90
5	20.2	79.8	3.0	11.4	.4	18.0	79.5	2.1	1.87
6	0.0	100.0	2.8	9 9	4	0.0	90 B	0.0	

TARLE III

Composition of Catalysts, Series 3. Compare Fig. 4

Composition referred to 100 g. of anhydrous sample Available Remainder									
No.	MnO_x	CuO	H_2O	oxygen	CO ₂	MnO_2	CnO	MnO	x
1	100.0	0.0	3.8	16.2	trace	88.3	0.0	11.7	1.85
2	66.0	34.0	5.8	13.6	4.1	56.3	32.6	7.0	1.86
3	43.7	56.3	7.8	11.1	6.7	31.8	52.5	9.0	1.74
4	36.7	63.3	8.2	10.2	6.0	23.0	59.5	11.5	1.62
5	28.5	71.5	9.8	10.1	9.8	19.5	64.5	6.2	1.72
6	0.0	100.0	9.5	9.3	7.0	0.0	93.0	0.0	

dioxide, No. 1, did not reach this efficiency until the temperature was raised to 160° and 280°, respectively.

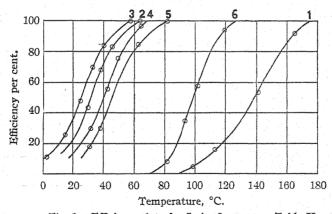


Fig. 3.—Efficiency data for Series 2; compare Table II

A comparison of Figs. 2 and 3 shows a distinct improvement in efficiency for the catalysts of Series 2, over the corresponding ones of Series 1. This is probably due to the fact that the oxides of Series 2 were washed free from soluble salts.

In Fig. 4 the results for Series 3, except for the poor efficiency of the basic copper carbonate, No. 6, are seen to be in close agreement with those for Series 2, Fig. 3. It is remarkable that the relatively high carbon dioxide content (see Table III) of the mixtures has so little effect. The water

content is also higher than in Series 2, but there is no reason to suspect that the catalysts were not operating in the region of maximum efficiency (compare the following section). In this series, as in the two earlier ones, the catalyst whose composition is closest to 60% of MnO_x and 40% of cupric oxide (No. 2 in this case) is the most active; but the difference between it and the other mixtures in the series is not great.

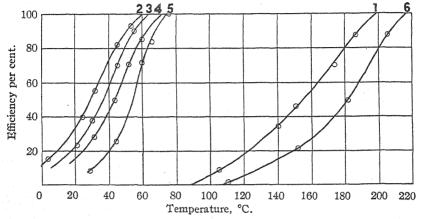


Fig. 4.—Efficiency data for Series 3; compare Table III

The efficiency-temperature curves for the Washington catalysts, Nos. 1 and 6, Fig. 5, correspond closely with those for Nos. 1 and 6 of Series 2, Fig. 3, for which the methods of preparation were similar. But the mixture, W3 (Curve 3), is a far more active catalyst than any of our mixtures;

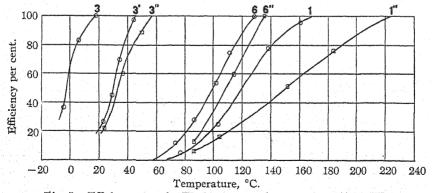


Fig. 5.—Efficiency data for Washington catalysts; compare Table IV

it operated at 100% efficiency below 20° , while no other did so below 55° . The analytical data in Table IV show that this catalyst is remarkable for the high content of oxygen in its MnO_x ; the value of x, 1.95, is higher than in any other sample. Its carbon dioxide content is relatively low (compare

Nos. 2 and 3, Table III). These facts suggest that there was some unknown but essential difference in the methods of preparing the constituents of this catalyst, but we do not know whether its high activity is to be attributed to such an explanation, or to the fact that the moist mixture of the constituents was subjected to high pressure. The data of Merrill and Scalione¹³ on the effect of pressure on the "life" of the catalyst in moist air probably do not throw any light on this question.

TABLE IV

COMPOSITION OF WASHINGTON CATALYSTS. COMPARE FIG. 5

Composition referred to 100 g. of anhydrous sample

		Available Remainder							
No.	MnO_x	CuO	H_2O	oxygen	CO_2	MnO_2	CuO	MnO	x
1	100	0.0	15.2	15.6	trace	85.0	0.0	15.0	1.82
3	52.8	47.2	6.2	13.6	3.6	48.9	45.5	2.0	1.95
6	0.0	100.0	2.9	10.0	trace	0.0	100.0	0.0	
1'	100.0	0.0	10.5	14.6	trace	• •			
1"	100.0	0.0	2.4	13.4	trace				
3'	52.8	47.2	12.4	13.6	3.9				
3"	52.8	47.2	4.3	12.8	trace	• •			
6'	0.0	100.0	3.7	10.0	trace	• • •			
6"	0.0	100.0	2.2	10.1	trace				

Variation of the Water and Oxygen Contents of the Catalysts

Other investigators have found that partial dehydration of the oxide catalysts is necessary in order to make them appreciably active. A rapid increase in activity is caused by the initial removal of water. This rate of increase, however, does not continue indefinitely, for a region is reached such that further slow dehydration causes a comparatively slight change in the activity. For example, in the case of Catalyst 3, Series 1 (approximately 60% of manganese dioxide and 40% of cupric oxide) a decrease in the water content from 12% to 7.5% (referred to the water-free material) reduced the temperature required for 50% efficiency only from $49\degree$ to $45\degree$. The removal of water up to this point did not cause an appreciable decrease in the oxygen content of the catalyst.

Reference to the tables of the preceding section shows that the water content of the mixed catalysts did not differ greatly within a given series, and was for each catalyst probably in the region where the change of activity with dehydration was slight. Since all were submitted to a similar drying process, the variation of the water content indicates the relative ease with which each lost water. In Series 1 and 2 the manganese dioxide was the more hydrated and the water content of the mixtures decreased with the manganese dioxide content. In Series 3 there was a trend in the opposite direction because the basic copper carbonate contained the more water.

¹³ Ref. 3, p. 1995, Table III.

It was found that continued drying of the catalyst, beyond the region referred to above, resulted in decreased activity, and loss of oxygen except in the case of copper oxide. A sample of the Washington mixture, No. 3" Table IV and Fig. 5, was dried over a moving flame for a short time. Comparison with No. 3 shows a great lowering of activity when the water content had been changed from 6.2 to 4.3 and the oxygen content lowered from 13.6 to 12.8. Another example of the loss of a small amount of oxygen in drying is furnished by the results for No. 3, Series 1 in Table V below. Data for the Washington samples of copper oxide and manganese dioxide are given in Table IV and Fig. 5. The efficiency of a sample of copper oxide, No. 6', which contained 3.7% of water was found to be coincident with Curve 6 (2.9% of water); but the activity was ultimately reduced by further drying at a higher temperature (compare No. 6"). The oxygen content was unchanged. In the case of the manganese dioxide loss of oxygen occurred before the decrease in activity. Thus, No. 1', which had been dried under suction for two hours at 200° and contained 10.5% of water, showed an efficiency corresponding to Curve 1 (15.2% of water), although its oxygen content had been changed from 15.6 to 14.6. Continued drying at higher temperature reduced the efficiency to that represented by Curve 1", and lowered the oxygen content to 13.4. It seems probable from these results that the decrease in activity finally obtained is due to a change of structure. The active mixed catalyst is sensitive to loss of oxygen, while the much less active manganese dioxide is not.

The high oxygen content of the most active catalyst, W3, has already been referred to and, as implied in the preceding paragraph, it is possible that there is a relation between the content of available oxygen of a mixed catalyst and its activity. However, even if this should prove to be true, oxygen comparisons would have to be restricted to samples of the same catalyst which had been subjected to various treatments. From our data for Series 1 to 3 we have found no relation between the values of x, Tables I to III, and the relative activities of the various catalysts.

Merrill and Scalione considered that the oxygen content of a catalyst is one of the variables at the steady state, and reported¹⁴ that the catalyst, when operating at low efficiency with either dry or wet gas, lost oxygen which was restored by operation at higher efficiency. We, however, have been unable to check this result. In each of the four sets of experiments in Table V, the oxygen content is seen to be practically the same whether the catalyst was operated at low or high efficiency. In each experiment the catalyst was operated for from one hour to two hours with dry gas at the efficiency stated before a sample was taken for analysis. These results are not conclusive, since the amount of oxygen that could be removed in one hour from a catalyst operating at low efficiency with 0.2% to 0.4% of

¹⁴ Ref. 3, pp. 1993 and 1997.

carbon monoxide does not exceed the possible limit of error in the analysis. But our failure to detect an increase of the oxygen content in any sample of a catalyst operating at high efficiency, and the result given in a later section that the speed of reduction is slower than the speed of catalysis, make it probable that there is no appreciable change in the oxygen content of the catalyst.

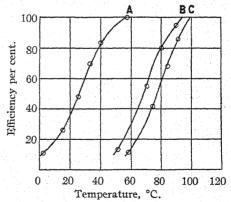
TABLE V OXYGEN CONTENT OF CATALYSTS

	Last op	Last operated at		
CO %	Temp.	Efficiency %	Available oxygen	
0.17	62	93	12.24	
	41	32	12.18	
		25	12.22	
.20	64	100	11.92	
	41	33	12.04	
.23	70	100	11.70	
	30	4	11.69	
.38	60	100	12.82	
	30	40	12.90	
	.20	CO % Temp. 0.17 62 41 .20 64 41 .23 70 30 .38 60	CO Temp. 8 Efficiency % 0.17 62 93 41 32 25 .20 64 100 41 33 .23 70 100 30 4 .38 60 100	

Tests with Moist Gas

The effect of moisture on the operation of these catalysts has been studied extensively by the earlier investigators. For example, Merrill and

Scalione¹⁵ gave efficiency-temperature curves for gas of varying humidity, which show that the water vapor causes a decided decrease in activity. From these and other results, they concluded that the moisture absorbed from the gas remains for the most part as a film on the surface of the catalyst, hindering the adsorption of carbon monoxide and oxygen, and does not re-hydrate the oxides to any considerable extent. This film was removed by Fig. 6.—Efficiency-temperature curves for dry operation with dry gas at higher



and moist gas

temperatures and the catalyst gradually regained its former activity.

In order to check these observations and to obtain comparable efficiency-temperature curves for dry and moist gas, some tests were made on Catalyst 2 of Series 2. Vapor pressures of 11.5 mm. and 5.1 mm. were obtained by allowing 44% and 58% sulfuric acid solutions to drip through the bead tower. The steady-state points were obtained as in the dry gas tests

¹⁵ Ref. 3, p. 1998.

and were found to be quite reproducible whether approached from higher or lower efficiencies. Contrary to the results of Merrill and Scalione, no decrease in the oxygen content was detected for samples which had been operating at low efficiencies. In Fig. 6, A represents the efficiency for dry gas, B for water-vapor pressure of 5.1 mm. and C for vapor pressure of 11.5 mm.

The fact that water vapor is strongly adsorbed and tends to form a film on the surface of the catalyst, indicates that this equilibrium film is the retarding factor which accounts for the decreased efficiency of the catalyst with moist gas. The similar form of the curves for moist gas and dry gas suggested the presence of a strongly adsorbed film, when operating with dry gas also, which might be the limiting factor in the catalysis. It seemed likely that carbon dioxide would be the more strongly adsorbed, of the gases concerned and would, therefore, be more apt to exert such a covering action. It was thought that the addition of carbon dioxide to the testing gas might cause a decrease in efficiency, if the catalyst had a tendency to take on such a film of carbon dioxide. However, the results of some experiments on Catalyst 3 of Series 2, with a partial pressure of carbon dioxide of 1/3 atmosphere, indicated that there was no marked effect. Since in the absence of added carbon dioxide the partial pressure of carbon dioxide in the gas leaving a catalyst operating at 100% efficiency would be only 0.002 atmosphere, it follows that an increase in the carbon dioxide pressure of 167 fold (or more when the catalyst is operating at lower efficiency) has little or no effect. This result does not prove that there is no protective film of carbon dioxide, but simply that such a film, if it exists, is not in equilibrium with the surrounding gas. In other words, this is a question of rate and not of equilibrium, and it is possible that the carbon dioxide is given off so slowly by a catalyst operating at low efficiency that a film is built up at the steady state. Definite evidence in favor of this mechanism will be presented in a later paper.

The Reduction of the Catalyst by Carbon Monoxide

The probability that the oxygen content of a catalyst remains practically constant has already been mentioned. In order to obtain data on the ease of reduction of the catalysts some runs were made with a mixture of about 1% of carbon monoxide in nitrogen. Oxygen was removed by means of yellow phosphorus, and the mixture was passed through the catalyst at the rate of 300 cc. per minute. Air was admitted to the gas stream after passing the catalyst in order that the analyzing device might be used to measure the change in the carbon monoxide content of the gas; the rate of flow of air was maintained constant at about 420 cc. per minute by means of another flowmeter. Before an experiment was begun nitrogen was passed through the system for half an hour to sweep out oxygen.

The behavior of Catalyst 3 of Series 2 was typical for all experiments started at a temperature close to that at which the catalyst operated at 99-100% efficiency with carbon monoxide in air, and will be described in detail. The experiment was begun with the catalyst at a temperature of 56° (compare Fig. 3), and its behavior is shown graphically in Fig. 7.

The initial reading of 23.0 corresponds to the concentration of carbon monoxide in the nitrogen mixture, which was 0.86% as determined by the iodine pentoxide method. When the gas was turned through the catalyst (fourth minute) the drop in the reading indicated a very rapid reaction and the temperature of the catalyst rose from 56° to 63° during the first 9 minutes. As shown by the curve the rate of carbon monoxide oxidation then became progressively slower and seemed to be practically constant between the times 40 and 65 minutes. The catalyst temperature had now returned to 58° . Between the times 65 and 85 minutes the temperature of the catalyst was raised to 86° and the decreasing deflections showed that

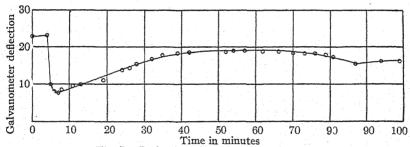


Fig. 7.—Reduction of catalyst by carbon monoxide

carbon monoxide was then being oxidized, at the expense of the catalyst, more rapidly at the higher temperatures. While the rate of this reaction and the temperature were still increasing the input of heat was decreased; this corresponded to the gradual rise of the curve, indicating at the end of the experiment 22% oxidation at a temperature of 84° .

A sample of the catalyst taken immediately after the run showed a loss of 16.3 mg. of oxygen per gram of the anhydrous sample, which corresponds to about 10% of the available oxygen originally present. From the amount of carbon monoxide oxidized during the run, and the weight of the sample, 1.38 g., an approximate calculation of the oxygen loss was made, which agreed fairly well with the above figure, thus showing that the gas mixture was practically free from oxygen. It was found that, unless extreme precautions were taken to remove all the oxygen, the carbon monoxide combined with this oxygen in preference to reducing the catalyst.

The partially reduced catalyst was then treated with the usual mixture of carbon monoxide and air for two hours. It then showed an efficiency of but 10% at 55° and of 80% at 82° , while the same catalyst before reduction

was 100% efficient at 60°. Analysis of the sample showed that over half of the lost oxygen had been restored by this air treatment. The failure of the catalyst to return to its former state of activity, in spite of the partial restoration of oxygen, suggests that it had suffered a change of structure. The efficiency of the more active mixed Washington catalyst was also found to be permanently impaired by similar reduction (at 30–38°) with carbon monoxide, but in this case there was little evidence to indicate that any of the lost oxygen was regained in the subsequent operation of the catalyst with carbon monoxide in air. These results support the suggestion made in a previous section that the oxygen contents of samples of a given mixed catalyst may indicate the relative activity.

A similar experiment at a higher temperature (150–166°) with the manganese dioxide of Series 2 showed that its efficiency was not permanently lessened by reduction to the extent of 7% of its available oxygen. It returned to its former activity when treated with carbon monoxide and air, and analysis showed that most of the lost oxygen had been restored. It has already been pointed out above that the active manganese dioxide catalyst is not very sensitive with respect to a change in the oxygen content. Whether this fact and the restoration of the oxygen lost in reduction are due simply to the high temperature necessary for operation as a catalyst, or can be taken as evidence that the mixed catalysts possess a structure different from that of the one-component catalysts, we are unable to decide.

In the reduction experiment begun at a temperature at which the catalyst could act with 99 to 100% efficiency as a catalyst, there action was very fast only for the first few minutes, after which its speed decreased fairly rapidly. It follows that there is only a small supply of "active" oxygen at the surface of the catalyst, and that the removal of oxygen from the catalyst becomes increasingly difficult as the reaction proceeds. The speed of the latter slow reaction increases rapidly with the temperature, and hence must be negligible at low efficiency. Similarly, the initial reaction is slow when the experiment is started at these lower temperatures. The simplest explanation of the decrease of the rate as the reaction proceeds and as the temperature is lowered is that the solid surface is protected by a film which is then held more firmly.

Our results show that at a given temperature the catalytic process cannot be replaced by a series of alternate treatments with carbon monoxide and air, at least unless the duration of each single treatment is made very short. The simultaneous reaction of the catalyst with carbon monoxide and oxygen takes place more rapidly than the reaction with carbon monoxide alone at the same temperature.

Discussion of the Mixture Effect

The relation of the compositions of the catalysts to their activity is best shown by the temperature-composition diagram, Fig. 8. Here the ordinate

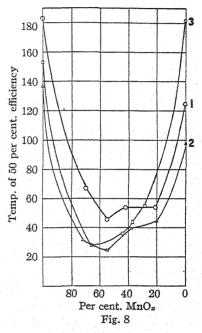
represents the temperature corresponding to 50% efficiency and the abscissa gives the percentage of MnO_x in the anhydrous mixture. The values of MnO_x were given in Tables I to III and the temperatures of 50% efficiency were read from Figs. 2 to 4. The numbers 1, 2 and 3 at the right-hand side of the figure refer to the three different series.

The striking result is the rapid increase, in all cases, of the activity of the one-component catalyst on the addition of small amounts of the second component. Evidence is therefore lacking of any fundamental difference between this example of co-activation of catalysts, and the promoter action

of an inert substance on a catalyst. Our results also indicate that the mixture of 60% of MnO_x and 40% of cupric oxide is but slightly more active than other mixtures, and that basic copper carbonate as a component has little, if any, advantage over copper hydroxide.

The following theory of the mixture effect in this case, which was developed early in the investigation, proved useful throughout our work, and will be discussed in connection with additional evidence in a later paper.

By the action of carbon monoxide and oxygen a protective film is formed on the catalyst which interferes with further action, unless it can be rapidly desorbed as carbon dioxide. The film builds up to a lesser extent for mixtures than for the one-component catalysts at the same temperature.



The slow limiting reaction may be the rate of desorption of carbon dioxide or the rate of a transformation within the film. We could stop with the statement that this is a question of the structure of the catalyst, but it seemed worth while to seek an interpretation in terms of valence theory.

The porous granules are believed to consist of a network of chains of atoms held together by valence forces. ¹⁶ The forces that come into play

16 Compare Langmuir, This Journal, 38, 2285 (1916).

The formation of the firm porous granule from the hydrated oxide or oxides may be thought of as follows. Each hydrated oxide is precipitated in the form of minute particles, the size of which is determined by the method of precipitation, but is greater than molecular dimensions. The filter cake, before it is dried consists of particles surrounded by films of water, which enable the relative positions of the particles to be easily changed for example, in a kneading process. In the preliminary drying as the water is slowly expelled, the particles are gradually drawn together, and in many places contact is suffi-

at or in the film are also valence forces. When the catalyst contains the two oxides, they will tend to neutralize each other's valence forces, since they differ in basicity or polarity, and the strength of the valence forces at the film may be expected to be less than for a one-component catalyst. In other words, an increase in the rate of desorption, or increase in the rate of a reaction within the film, is attributed to what may be considered a partial chemical reaction between the two oxides.

Summary

Temperature-efficiency curves have been obtained for three series of partially hydrated, porous catalysts of manganese dioxide and cupric oxide. Pronounced improvement in activity is caused by the addition of a small amount of either oxide to the other.

Partial dehydration is necessary to bring a catalyst to the region of maximum activity, but the water content may then be lowered to a relatively small value by slow dehydration with but little change in the efficiency. Continued dehydration, however, finally lowers the efficiency, and causes loss of oxygen (except in the case of copper oxide).

The efficiency of a catalyst is independent of the carbon monoxide concentration between 0.1 and 0.6%, and is practically unchanged by the presence at high concentration of carbon dioxide, the product of the reaction.

Water vapor has a marked poisoning effect, which is reversible.

It is probable that under steady-state conditions the oxygen content of a catalyst is practically constant whether the catalyst is operating at low or high efficiency.

A catalyst is reduced when treated with carbon monoxide in the absence of oxygen at a temperature at which it would act as a catalyst. The activity of a mixed catalyst is permanently impaired by this reduction, even when much of the lost oxygen is restored on subsequent operation as a catalyst.

A theory for the mixture effect in this case has been suggested.

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ciently close to allow valence forces to come into play between the molecules of different particles. The plastic material has now been transformed into a solid. Finally, as the water of hydration is gradually expelled, the body becomes porous.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SOUTHERN BRANCH OF THE UNIVERSITY OF CALIFORNIA]

THE VAPOR PRESSURE OF MONATOMIC ELEMENTS

By Russell W. Millar Received July 23, 1923

The differential equation, $\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$, which expresses the change of va-

por pressure with the temperature in terms of the heat of vaporization and the change of volume, has been integrated heretofore for the purpose of obtaining a vapor-pressure equation. The equation derived contained a "chemical constant" which depended only upon the element under consideration. This constant was determined from the quantum theory, from the relation of Nernst, $C = -1.60 + 1.5 \log w$, where w is the molecular weight of the monatomic gas, or most accurately from two vapor-pressure measurements. It was then possible, using either of the first two methods of determining the chemical constant, to construct an entire vapor-pressure curve from specific heat data of the condensed phase and one point on the vapor-pressure curve.

Investigators² who have provided us with a method of calculating the entropy of a monatomic gas have made possible a simple and straightforward integration of the differential equation. The expression obtained is probably more convenient than that of Nernst for the purpose of calculating vapor pressures in unexplored ranges of temperature.

If we neglect the volume of the condensed phase and let V represent the molar volume of the gas, and assume that pV = RT, we have, from the above

$$\frac{\mathrm{d}\ln p}{\mathrm{d}\ln T} = \frac{\Delta H}{RT} = \frac{\Delta S}{R},\tag{1}$$

an equation used recently by Hildebrand.³ ΔS is the entropy of vaporization, namely $S_g - S_c$, where S_g is the entropy of the gas and S_c that of the condensed phase.

If we express p in atmospheres, then we have from Lewis' theory of ultimate rational units

$$S_g = R \ln (T^6/2w^3/2/p) - 2.63$$
 (2)

where w is the molecular weight of the gas. Also

$$S_c = S_0 + \int_{T_0}^T C_p \, \mathrm{d} \ln T,$$

¹ Nernst, "Theoretische Chemie," Macmillan and Co., 7th ed., 1916, pp. 236, 756. F. Born, Ann. Physik, 69, 473 (1922). Trautz and Stäckel, Z. anorg. Chem., 122, 81 (1922). Henglein, ibid., 123, 137 (1922).

² Sackur, Ann. Physik, [4] **36**, 598 (1911); **40**, 67 (1913). Tetrode, ibid., [4] **38**, 434 (1912). Lewis, Phys. Rev., [2] **18**, 121 (1921).

³ Hildebrand, This Journal, 37, 970 (1915).

⁴ Lewis, Gibson and Latimer, *ibid.*, 44, 1008 (1922).

neglecting the effect of change of pressure upon the entropy of the condensed phase. Here S_c is the entropy of the condensed phase at some temperature T_0 , and C_p is its molar heat capacity at constant pressure. Now C_p must be expressed as some function of the temperature which will be integrable in the expression above and also give a result which will leave Equation 1 integrable. The simplest function is $C_p = \alpha + \beta \ln T + \gamma (\ln T)^2$. Of course, this function does not express exactly the relation between C_p and T over any extended temperature range, yet it was found that quite accurate calculations of vapor pressure over temperature ranges sufficiently long could be made when γ , and even in some cases β , were omitted. Omitting γ , the inclusion of which, however, in no way complicates the integration of Equation 1, we obtain

$$S_c = S_0 + \alpha \ln T + \frac{\beta}{2} (\ln T)^2 - \alpha \ln T_0 - \frac{\beta}{2} (\ln T_0)^2$$
 (3)

Substituting Equations 2 and 3 in 1, we have

$$\frac{\mathrm{d} \ln p}{\mathrm{d} \ln T} + \ln p = \left(2.5 - \frac{\alpha}{R}\right) \ln T - \frac{\beta}{2R} (\ln T)^2 + \frac{1}{R} \left[1.5 R \ln w + \alpha \ln T_0 + \frac{\beta}{2} (\ln T_0)^2 - 2.63 - S_0\right]$$

This is a differential equation linear with respect to the dependent variable and of the form $\frac{dy}{dx} + y = ax - bx^2 + K$, of which the solution is $y = (a + 2b)x - bx^2 + Ze^{-x} - a + 2b + K$, where Z is the constant of integration. Likewise

$$\ln p = \left(2.5 - \frac{\alpha - \beta}{R}\right) \ln T - \frac{\beta}{2R} (\ln T)^2 + \frac{Z}{T} - \left(2.5 - \frac{\alpha - \beta}{R}\right) + \frac{1}{R} \left[1.5 R \ln w + \alpha \ln T_0 + \frac{\beta}{2} (\ln T_0)^2 - 2.63 - S_0\right]$$

Using common logarithms, we have

$$\log p_{\text{atm.}} = \left(2.5 - \frac{\alpha - \beta}{R}\right) \log T - \frac{2.303 \,\beta}{2R} (\log T)^2 + \frac{Z}{T} + \frac{1}{R} \left[1.5 \,R \log w + \alpha \log T_0 + \frac{2.303 \,\beta}{2} (\log T_0)^2 - \frac{2.63 + S_0 - (\alpha - \beta) + 2.5R}{2.303}\right]$$

Therefore, if, for a condensed phase of any element which vaporizes to a monatomic gas, we know the values of α , β , and the entropy S_0 at some temperature T_0 , and one vapor-pressure measurement, such as the boiling or sublimation point, by means of which Z may be evaluated, the complete vapor-pressure curve for that phase over the temperature range for which α and β are valid may be calculated.

In Table I the calculated values for mercury, sodium, zinc and hydrogen have been compared with the observed values of various investigators. These calculations will now be made to illustrate the use of the equation. The elements named do not by any means exhaust the number of those for which the necessary data exist.

Mercury.—According to Barnes,⁵ the heat capacity of mercury above 120° is about 6.65. Taking this value as constant, and taking with Lewis, Gibson and Latimer $S_0 = 17.81$ at $T_0 = 298^{\circ}$ A., and from Smith and Menzies⁶ the value of the boiling point, 357° C., we obtain

$$\log p_{\text{mm}} = -0.8443 \log T - \frac{3319.6}{T} + 10.5134 \tag{4}$$

Since the heat capacity of mercury increases slightly with decreasing temperature below $160\,^{\circ}\text{C}$., a new equation was used below $120\,^{\circ}\text{C}$. to calculate the vapor pressure at temperatures as far down as the freezing point. In this range Barnes⁵ gives $C_p = 6.70$ (average), and we may take the same value of S_0 and T_0 as before. In order to calculate Z we may take either the calculated or observed value of p. Taking the latter as $0.829\,$ mm. at $394.9\,^{\circ}\text{A}$, we obtain a slightly different equation:

$$\log p_{\text{mm}} = -0.8694 \log T - \frac{3320.2}{T} + 10.5838 \tag{5}$$

which we can use below 120°C. The values given by this equation are slightly higher than those given by the preceding equation in the lower range of temperature. The results are as accurate as the value of the heat capacity chosen, which, though an average, differs but little from the extreme values.

We are now in a position to calculate the vapor pressure of solid mercury. The data of Pollitzer⁷ for the heat capacity of solid mercury from about 60° A. to the melting point may be expressed with considerable accuracy by $C_p = 1.118 + 1.016$ ln T. At the melting point, $T_0 = 234.1$, $S_0 = 13.80$. Evaluating Z from the calculated value of p at 234.1° A., we obtain

$$\log p_{\text{mm}} = 1.4487 \log T - 0.5882 (\log T)^2 - \frac{3621.7}{T} + 9.6814$$
 (6)

for solid mercury. At the temperature of boiling liquid air, about 90°A., we find $p = 1 \times 10^{-30}$ mm.

Sodium.—E. Griffiths, and Griffiths and Griffiths have measured the heat capacity of sodium for a short distance above the melting point. In the absence of more data, the equation $C_p = 7.40$ has been assumed to hold throughout the range to the boiling point. Using Lewis, Gibson and Latimer's value, $S_{298} = 12.2$, calculating $S_{370.6} - S_{298} = 1.5$ from the data of E. Griffiths and using Iitaka's value of the entropy of fusion, $\Delta s = 1.6$, we obtain at the melting point, $T_0 = 370.6$ °A., $S_0 = 15.3$ for liquid sodium. Gebhardt¹¹ gives, at T = 813°A., p = 18.5 mm.

- 5 Barnes. Rept. Brit. Assoc. Winnipeg, 1909, p. 403.
- 6 Smith and Menzies, THIS JOURNAL, 32, 1434 (1910).
- 7 Pollitzer, Z. Elektrochem., 19, 513 (1913).
- 8 E. Griffiths, Proc. Roy. Soc., 89A, 561 (1914).
- 9 Griffiths and Griffiths, Phil. Trans. Roy. Soc., 213A, 119 (1913).
- 10 Iitaka, Sci. Rep. Tôhoku Imp. Univ., 8, 99 (1919).
- 11 Gebhardt, Dissertation, Erlangen, 1903.

The equation then becomes

$$\log p_{\rm mm.} = -1.20 \log T - \frac{5135}{T} + 11.071 \tag{7}$$

For solid sodium we obtain from E. Griffiths $C_p = -20.2808 + 4.6869$ lnT, an equation which reproduces the results fairly accurately from room temperature to the melting point. Taking T_0 as equal to the melting point 370.6°A., $S_0 = 13.7$, and evaluating Z from the calculated value of p at 370.6°A., we obtain

log
$$p_{\text{mm}}$$
. = 15.0560 log T —2.7136 (log T)² - $\frac{7091.9}{T}$ - 4.6050 (8)

This equation gives $p = 1.7 \times 10^{-8}$ mm. at 298°A.

Zinc.—According to Iitaka,¹⁰ the heat capacity of liquid zinc is 7.91 and is nearly independent of the temperature. The same observer gives 2.19 as the entropy of fusion. Using his data for the heat capacity of solid zinc from 298°A. to the melting point, and $S_{298} = 9.83$ as given by Lewis, Gibson and Latimer, we obtain $S_0 = 17.46$ for liquid zinc at the melting point, $T_0 = 692$ °A. The boiling point of zinc is taken as 1193°A. From these data we obtain

$$\log p_{\text{mm}} = -1.4779 \log T - \frac{68336}{T} + 13.1558 \tag{9}$$

Iitaka's values of the heat capacity of zinc from room temperature to the melting point are fairly well represented by $C_p = -1.7437 + 1.3550$ ln T. Taking $T_0 = 298$ °A., $S_0 = 9.83$, and the vapor pressure at the melting point as calculated from Equation 9 we obtain

$$\log p_{\text{mm}} = 4.0583 \log T - 0.7845 (\log T)^2 - \frac{6823.1}{T} + 3.7555 \tag{10}$$

Hydrogen.—According to Eucken,¹² the heat capacity of hydrogen gas below 60°A. is that of a monatomic gas, and consequently Lewis, Gibson and Latimer⁴ have applied the Sackur equation to the calculation of the entropy of hydrogen gas at the boiling point. If that application is valid, we are justified in using the method of this paper to calculate the vapor pressure of hydrogen.

Keesom and Onnes, ¹⁸ and Eucken ¹² give consistent values for the heat capacity of liquid hydrogen which may be represented closely by $C_p = -6.14 + 3.55 \ ln \ T$. Keesom and Onnes ¹⁸ measurements of the heat capacity of solid hydrogen give 0.6 as the molar entropy of hydrogen at the melting point, 14°A. The same authors, and also Dewar, ¹⁴ have determined the molar heat of fusion of hydrogen to be about 30, from which we find 2.14 as the entropy of fusion. Taking, then, $S_0 = 3.00$ at

¹² Eucken, Ber. physik. Ges., 18, 4 (1916).

¹³ Keesom and Onnes, Comm. Phys. Lab. Leiden, 153a (1917).

¹⁴ Dewar, J. Chem. Soc., 73, 528 (1898).

 $T_0 = 14$ °A., and Cath and Onnes' 15 boiling point, 20.39 °A., we obtain

$$\log p_{\text{mm}} = 7.3725 \log T - 2.0572 (\log T)^2 - \frac{26.8679}{T} - 1.9280$$
 (11)

The values given by this equation do not, however, agree with the experimental values of Keesom and Onnes.

It will be noted that the vapor-pressure equation is of the form, $\log p = A \log T + B(\log T)^2 + \frac{Z}{T} + C$, and that A and B are determined solely by the heat-capacity curve of the condensed phase, here liquid hydrogen. If Keesom and Onnes' and Eucken's determinations of this curve are correct, and if, indeed, the application of the Sackur equation to gaseous hydrogen at these temperatures is valid, we should be able to obtain a vapor-pressure equation by evaluating both Z and C by means of two determinations of the vapor pressure. It will be noted that here we are not depending upon any of the experimental determinations of the heat

capacity of solid hydrogen and the heat of fusion of hydrogen, since S_0 occurs only in the constant C. The equation obtained by this method is

$$\log p_{\text{mm}} = 7.3715 \log T - 2.0572 (\log T)^2 - \frac{40.733}{T} - 1.2537$$
 (12)

It will be noted in Table I that the calculations from this equation agree with the determinations of Keesom and Onnes but little better than those from Equation 11. The failure of Equation 12 indicates that the Sackur equation is not applicable, that the heat-capacity measurements of Keesom and Onnes are uncertain, or that the vapor-pressure measurements are themselves uncertain, or a combination of these circumstances.

Finally, a calculation of the heat of fusion was made on the assumption that Keesom and Onnes' values of the vapor pressure and the heat capacity of the solid are correct, and that the application of the Sackur equation is valid. From the last we calculate the entropy of gaseous hydrogen in equilibrium with the solid at the melting point, $14^{\circ}A$. The pressure, as extrapolated beyond the last value of Onnes at $14.2^{\circ}A$., is 55.27 mm. We obtain $S_{\rm gas}=17.29$. From the vapor-pressure curve the entropy of vaporization is 15.34 at $14^{\circ}A$. If the entropy of solid hydrogen at the melting point is 0.6, then the entropy of fusion is 17.29—(0.6+15.34)=1.35, and the heat of fusion is 18.9 cal./mole.

It will be noted that the calculated values are as accurate as the specificheat data used in the formulas, and in the case of the best known vaporpressure measurements, namely, those of mercury, the agreement between the observed and calculated values is best. Unfortunately, the values of the specific heats in the neighborhood of the boiling points are extrapolated over a long range, so that accurate values of the heats and entropies of vaporization at the boiling points cannot be calculated.

¹⁵ Cath and Onnes, Comm. Phys. Lab. Leiden, 152a (1917).

Of course the same method can be used to calculate the partial pressure at a series of temperatures of a monatomic gas in equilibrium with any solid or liquid phase of constant composition for which the specific-heat curve and entropy are known, providing one value of the partial pressure is known.

Table I
Calculated and Observed Values of Vapor Pressure in Millimeters

(Calculat	red and (DBSERVED VAL	ues of Vapor I	Pressure in	MILLIMETERS
Equati	on t	T	⊅(calc.) Millar	p(calc.) others	p(obs.)	Observer or calculator
				Mercury		
4	458	731	3582.5	3611.7		
	444	717	2969	2990		
	434.7	707.8	2611.5		2624.3	
	417.2	690.3	2036.6		2037.2	Smith and Men-
	404.3	677.4	1670.7		1675.3	zies ⁶
	372.7	645.8	1001.2		1002.5	
	357	630.1	(760)		760	
•	254	527	82.4		82.08	
	191.5	464.6	13.08		13.02	1.
	150.0	423.1	2.812		2.802	Menzies ¹⁶
	121.8	394.9	0.822		0.829	j .
5	30	303	.00290	0.00299	0.00278	Calculations
	25	298	.001955	.001995		S. and M.
	20	293	.00126	.00131	.00188	Observations
	0	273	.032033	.03207	.0,184	Knudson ¹⁷
	- 39	234.1	.0,228			
		m. p.				
6	-183	90	10-30			
				Sodium		
7	861	1134	760		760)
	858	1131	740			
	857	1130	731			
	727	1000	217			
	570	843	29.0		80.0	·
	560	833	25.4		33.2	9
	550	823	21.4		23.0	Gebhardt ¹¹
	540	813	(18.5)		18.5	Kröner ¹⁸
	520	793	13.2		12.4	
	500	773	9,0		8.6	
	480	753	6.2		6.1	
	460	733	4.2		4.2	
	440	713	2.8		2.9	
	360	633	0.39		0.32	
	97.5	370.6	14×10 ⁻⁷			
		m. p.				
8	25	298	17×10^{-9}			
				7		
_	1510	1500		ZINC		
9	1510	1783	42.7 atm.		53 atm.	
	1280	1553	14.2		21.5	Greenwood ¹⁹
	1230	1503	10.7		14.2	
	1120	1393	5.3		6.3	

	920 750 500 419	1193 1023 773 692 m. p.	(760 mm.) 106 1.06 0.121	(760 mm.) 100 1	}	Johnston ²⁰
10	363 331 312 280 257 25	636 604 585 553 530 298	$\begin{array}{c} 0.0174\\.00476\\.00206\\.00044\\.000130\\1.25\times 10^{-14} \end{array}$,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	0.018 .0052 .0021 .00042 [.00012]	Edgerton ²¹
			H	YDROGEN		
11	• • • •	33.18 20.39 14.2	6.8 atm. (760 mm.) 88		12.9 atm. 760 mm. 61.80	
12	•••	33.18 31.36 20.39	12.1 atm. (7484.2 mm.) (760 mm.)	••••••	12.9 atm. 7484.2 mm. 760 mm.	Cath and Onnes ¹⁵
		14.2	43.8		61.80)

Summary

A formula has been derived by means of which the pressure of a monatomic gas in equilibrium with the liquid or solid element can be calculated from specific-heat data and one vapor-pressure measurement.

Sample calculations have been made for mercury, sodium, zinc and hidrogen.

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- 16 Menzies, This Journal, 41, 1783 (1919).
- ¹⁷ Knudson, Ann. Physik, **29**, 179 (1909). Hill, [Phys. Rev., **20**, 259 (1922)] gives 0.000350 mm. at 0°C., and 0.00273 mm. at 25°C.
 - 18 Kröner, Ann. Physik, [3] 40, 138 (1913).
 - 19 Greenwood, Proc. Roy. Soc. London, 83A, 483 (1910).
 - ²⁰ Johnston, J. Ind. Eng. Chem., 9, 873 (1917).
 - ²¹ Edgerton, Phil. Mag., 33, 33 (1917).

[Contribution from the Chemical Laboratory of the University of Illinois]

PROMOTER ACTION IN THE DECOMPOSITION OF POTASSIUM CHLORATE

By Harvey A. Neville Received July 26, 1923

Introduction

In an extensive research upon the catalytic decomposition of potassium chlorate¹ it was discovered that commercial manganese dioxide, or pyrolusite, was more active than the pure material in accelerating the evolution of oxygen. Analysis of the pyrolusite showed the presence of 8.8% of ferric oxide, Fe₂O₃, as an impurity. A mixture of pure manganese dioxide and ferric oxide in the proportions given by the analysis was then made and used as a catalyst. This mixture showed almost exactly the same activity as the pyrolusite, indicating that ferric oxide exerts a promoter action upon manganese dioxide in catalyzing the decomposition of potassium chlorate. The activities of these oxides separately and mixtures of the two as catalysts were measured at three different temperatures and the action of cupric oxide as a promoter with manganese dioxide was also studied.

Experimental Part

Apparatus.—The apparatus and method used in these experiments did not differ essentially from that described in other recent papers on this decomposition. The apparatus is indicated in Fig. 1. The reaction tube was heated by the condensation of

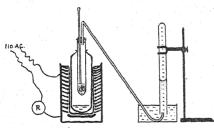


Fig. 1.—Apparatus

the vapor of a constant-boiling substance. The decomposition of potassium chlorate is exothermic and such a method of heating tends to act as a thermostatic arrangement; when the temperature of the reaction mass begins to rise above the boiling point of the liquid, heat is absorbed by the vaporization of liquid condensed on the reaction tube, which should be of thin glass for this reason.

Materials.—Fine crystals of the purest

potassium chlorate were used. The catalyst materials were finely ground pyrolusite, pure manganese dioxide made by the method of Georgen,² and cupric oxide made by oxidizing the pure metal, dissolving this oxide in nitric acid and decomposing the nitrate at 300°. Mixtures of catalysts were made both directly and by mixing the nitrate of one metal with the oxide of the other and heating to decomposition. The latter method gave more consistent results.

¹ The recent report of a similar investigation makes a complete presentation of results inadvisable at present. Compare Brown, Burrows and McLaughlin, This Journal, 45, 1343 (1923).

² Georgen, Compt. rend., 88, 797 (1879).

Procedure.—A sample for an experiment was prepared as follows. The potassium chlorate and catalyst in weighed proportions were finely ground, thoroughly mixed, moistened with water and dried. In this way the catalyst and potassium chlorate were brought into very intimate contact. A sample consisted of 6 g. of potassium chlorate plus an amount of the catalyst calculated as a certain percentage of the total weight. In the study of promoter action the catalyst was always 25%; that is, the mixture contained 6 g. of potassium chlorate and 2 g. of catalyst.

Results.—The results of the experiments at 328° are graphically represented in Figs. 2 and 3. The decomposition at this temperature is

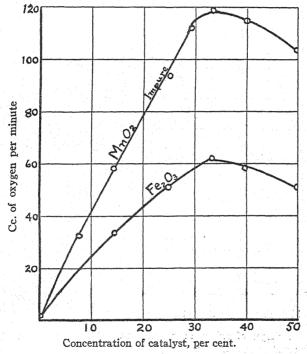


Fig. 2.—Rate of oxygen evolution with different amounts of catalyst

fairly steady and rapid and the temperature is safely below the melting point of potassium chlorate. At the other temperatures used (235° and 300°) the effects are exactly analogous, though less pronounced. The three oxides indicated are the only ones which have a marked catalytic activity at these temperatures. Above the melting point of potassium chlorate any finely divided solid accelerates the decomposition. As a basis for comparison it is to be noted that pure potassium chlorate at 328°, under the conditions of these experiments, evolves oxygen at the rate of 1 cc. per minute.

Discussion

The figures given for the rate of decomposition of potassium chlorate are not claimed as absolute values but are relative only. They are closely reproducible under the conditions of these experiments. The results obtained in any set of experiments will depend upon so many variable factors that no agreement will be possible except under those exact condi-

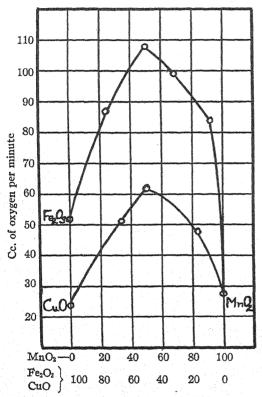


Fig. 3.—Percentages of oxides in mixture and rate of gas evolved at 328° from 6 g. of potassium chlorate mixed with 2 g. of catalyst

tions. Purity, melting point and previous treatment of the potassium chlorate, physical condition of the catalyst method of mixing and rate of heating are especially important factors.

In a recent article on promoter action A. Pickles³ suggested that if the atomic number of the metal present in a catalyst be even, the promoter should contain a metal of odd atomic number, and vice versa. A number of instances were cited where this is true. There are, however, many obvious exceptions, but it is apparent from a consideration of the law of probability that in 50% of all the cases of promoter action the rule must hold true even if there be no relation between atomic number and promoter action. The atomic numbers of the metals under consideration are Mn (25),

Fe (26), Cu (29)—so the rule holds in the combination Fe₂O₃-MnO₂, but does not in the case of CuO-MnO₂.

A comparison of Figs. 2 and 3 discloses the fact that while impure manganese dioxide is a much better catalyst than ferric oxide, the pure substance is slightly more than half as good but is very susceptible to promotion by ferric oxide. In Fig. 3 the fact that pure manganese dioxide and cupric oxide have about the same activity and nearly the same molecular weights would lead one to expect a 50–50 mixture of the two to give the

³ Pickles, Chem. Age (London), 8, 232 (1922).

best result. Such a mixture contains nearly twice as many molecules of manganese dioxide as of ferric oxide; and, although a molecule of ferric oxide is about four times as active as a molecule of manganese dioxide, this is balanced by the fact that the latter is more improved by a promoter than is the former.

Part of the experimental work for this paper was performed by Myron A. Snell, to whom acknowledgement is hereby made.

Summary

The fact that commercial manganese dioxide is a more effective catalyst than the c. p. material in the decomposition of potassium chlorate is ascribed to the presence of 8.8% of ferric oxide in the former.

Experiments with mixtures of these two oxides confirm this view and show that each oxide is a promoter for the other.

The action of cupric oxide and manganese dioxide as mutual promoters is also demonstrated.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF PROFESSOR EDWARD KREMERS]

A STUDY OF AMINO AND OXIMO DERIVATIVES OF THYMOQUINONE¹

By Ralph M. Hixon²

RECEIVED NOVEMBER 20, 1922

The study of the reaction of the amines with the quinones dates from the time of Hofmann's report³ of the isolation of a compound of the composition $C_6H_2O_2.N(C_6H_5)H$ from the reaction mixture of aniline and benzo-quinone. Some years later, the reaction was studied thoroughly by Zincke.⁴ He concluded that the amines reacted with the quinones in different ways under different conditions, giving the formulas of the following reaction products as proof of his statement.

Phenanthraquinone + methyl amine give $(C_{14}H_{18})(:N-CH_3)=0$ and $(C_{14}H_{18})(:N-CH_3)=0$ (1)

Phenanthraquinone + ammonia give (C₁₄H₁₈)(:N—H)=0 (2)

Benzoquinone + aniline give $(C_6H_2O_2)_2(NHC_6H_5)_2$ (3)

In 1881, Zincke⁵ concluded that the amines reacting with the quinones, replace a hydrogen atom of the quinone nucleus. This conclusion rested

- ¹ This communication is a portion of a thesis submitted to the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.
 - ² Fritzsche Brothers Fellow.
 - 3 Hofmann, Jahresber., 1863, 415.
 - 4 Zincke, Ber., 12, 1641 (1879).
 - ⁵ Zincke, Ber., 14, 92 (1881).

on the synthesis of the amine derivatives by reactions of the following type.

$$\begin{array}{c} O \\ CH_3 \longrightarrow Br \\ Br \longrightarrow C_3H_7 \end{array} + HNHCH_3 \longrightarrow \begin{array}{c} CH_3 \longrightarrow NHCH_3 + HBr \\ C_3H_7 \longrightarrow C_3H_7 \end{array}$$
 (4)

It should be noted that in drawing this conclusion, Zincke ignored the analyses of the phenanthraquinone derivatives which he had previously reported.

As a result of Zincke's work, the reactions of the amines with the quinones have been written as though direct union took place at the positions of the hydrogen atoms in the quinone nucleus. In 1901, Hofmann⁶ reported the following reaction for dibromo-thymoquinone with aniline.

$$\begin{array}{c} \text{Br} \longrightarrow \text{CH}_3 \\ \text{C}_3\text{H}_7 \longrightarrow \text{Br} \end{array} + \text{HNHC}_6\text{H}_5 \longrightarrow \begin{array}{c} \text{Br} \longrightarrow \text{NHC}_6\text{H}_3 + \text{CH}_4 \\ \text{C}_3\text{H}_7 \longrightarrow \text{Br} \end{array} \tag{5}$$

It will be seen that the reaction differs markedly from Reaction 4.

Considerable light is thrown upon the anomalous behavior of the quinones when their structure is compared to that of similar aliphatic compounds. The carbonyl group adds ammonia (or ammonia derivatives) to give addition compounds of the type = C(OH)NR₂; reference may be made to the aldehyde ammonia⁷ and to the stable compound described by Nef.⁸ Unsaturated aliphatic and aromatic compounds containing a carbonyl group may also add ammonia derivatives at the double bond⁹ as in the cases of the action of ammonia on certain unsaturated acids and the action of hydroxylamine on carvone.

In analogy to these reactions of ammonia derivatives with less complex compounds, the following reactions may be expected with the quinone nucleus under different conditions:¹⁰

- ⁶ Hofmann, Ber., 34, 1559 (1901). Böters, Ber., 35, 1502 (1902).
- ⁷ Richter-Smith, "Organic Chemistry," Blakiston, 8th ed., 1900, pp. 205-6.
- ⁸ Nef, Ann., 270, 267 (1922).
- ⁹ Weyl, "Methoden der organischen Chemie," Vol. I, p. 642.
- No The intermediate compound has been written in this form to show its analogy with the ammonia salts, such as NH₃.HCl. The existence of such union follows at once from consideration of the quinone structure in terms of the "Octet Theory." The cubical structure of Lewis and Langmuir has been avoided to prevent undue confusion, although their conclusions have played an important part in this study of thymoquinone.

The action of hydroxylamine upon the quinones and ammonia upon phenanthraquinone fall under type "a," but for most of the other reactions either "a" or "c" seems equally possible. The final product undoubtedly depends upon the basicity of the nitrogen derivative as well as upon the characteristics induced in the quinone nucleus by modifying its structure.

Thus dibromo-thymoquinone splits off hydrogen bromide in the expected way in the presence of the relatively strong base, monomethyl amine, but unexpectedly splits off methane with the weak base, aniline (see Reactions 4 and 5). McPherson and Dubois¹¹ have pointed out that the ketonic characteristics of the quinone carbonyl groups decrease with the introduction of negative groups in the quinone nucleus. The reaction of hydroxylamine with monohydroxy-thymoquinone to give monohydroxyamino-thymoquinone¹² instead of an oxime as was to be expected is to be explained by this decreased carbonyl characteristic and by the greater lability of the hydrogen induced by the presence of negative groups. Likewise, the action of hydroxylamine with dihydroxy-benzoquinone and monochloro-dihydroxy-benzoquinone reported by Kehrmann¹³ shows only one carbonyl group reacting to give an oxime, while one hydroxy group is replaced by an amino group in analogy to these reactions. Phenanthraquinone reacts with ammonia to give an imide,⁴ which would indicate an

¹¹ McPherson and Dubois, This Journal, 30, 816 (1908).

¹² Kowalski, Ber., 25, 1658 (1892).

¹³ Kehrmann and Tiesler, J. prakt. Chem., 41, 87 (1890).

intermediate addition compound similar to the aldehyde ammonia; in this connection it should be pointed out that the structure of phenanthraquinone is quite different from that of the true quinones, since the double bonds in the former are a part of neighboring phenyl rings and so are not capable of the rearrangements characteristic of the other quinones.

An intermediate addition compound similar to the ammonium salts in structure is indicated in Reaction 6; the possible existence of such compounds follows when the structure of the quinone is expressed according to the octet theories of Lewis and of Langmuir.¹⁰ Colorless crystalline addition compounds between amines and quinones have been frequently observed and various structures assigned to them; a summary of this work is given by Meyer and by Suide.¹⁴ The original work of Hebebrand¹⁵ on these compounds indicates that they have an ammonium structure.

It seemed possible that similar addition compounds would be formed by tertiary amines with the quinones which would be less apt to rearrange and, therefore, be more satisfactory for study. Examination of the literature gave but one confirmation of the existence of such compounds. Jackson and Clark¹⁶ state that dimethyl-aniline yielded colored addition products with all the quinones at their disposal. Most of these compounds were unstable but analyses were obtained for several which indicated union in equimolecular proportions.

Action of Dimethyl-aniline on Thymoquinone.—A few qualitative tests confirmed the statement of Jackson and Clark. It was found that thymoquinone dissolved in dimethyl-aniline with considerable absorption of heat; 8.2 g. of thymoquinone dissolved in two equivalents of dimethyl-aniline (12.1 g.) produced a drop in temperature from 23° to 10°, no precautions being taken to prevent the absorption of heat from external sources.

Although considerable time has been devoted to the study of this reaction, the conclusions are not definite. In the absence of solvents and oxidizing agents, including air, the mixture remains unchanged for months but in the presence of a solvent or of an oxidizing agent a purple tar is produced which is soluble in acids but decomposed by aqueous alkaline solutions. Saponification of the purple tar with 50% sulfuric acid yielded some dihydroxy-thymoquinone and the merest trace of monohydroxy-thymoquinone, which would seem to indicate that actual condensation had taken place just as between the primary and secondary amines and the quinones. The conclusion is not fully justified, however, until such a condensation product has been actually isolated. After the hydrolysis, small quantities of an intermediate crystalline compound (m. p. about

¹⁴ Suide, Ann., 416, 113 (1918).

¹⁵ Hebehrand, Ber., 15, 1973 (1882).

¹⁶ Jackson and Clark, Am. Chem. J., 34, 441 (1905).

 $140\,^{\circ}$ with decomposition) were isolated but could not be obtained pure enough for analysis. 17

From the structural standpoint of the octet theory, these addition reactions are analogous to the addition of tertiary amines with carboxyl chlorides¹⁸ and also to the addition reaction between the carbonyl group and phosphorus trichloride recently studied by Conant.¹⁹

Preparation of Nitroso-thymol and Nitroso-carvacrol.—The nitroso-thymol and nitroso-carvacrol were prepared in amounts of 200 g. each.²⁰ Directions for purifying these large quantities of crude materials follow.

- 1. Draw off as much as possible of the mother liquor with the aid of a suction pump, and wash the compound well with water. If the compound is dried without further purification, either in air or in a vacuum, it will become discolored in the course of a few days, oxides of nitrogen being slowly evolved in the decomposition. Preparations containing only a small amount of impurities show this decomposition.
- 2. Transfer the wet nitroso compound from the funnel to a large beaker and wash it twice with sufficient alcohol to form a thick paste; then remove as much of the alcohol as possible by means of a filter pump. An excess of alcohol should be avoided as the compound is quite soluble.
- 3. Remove the alcohol by washing the solid with a small amount of ether and dry the compound in a vacuum desiccator as rapidly as possible.
- 4. Beautiful crystals of nitroso-carvacrol can be obtained by crystallizing the dry compound from hot benzene. Benzene is also the best solvent for recrystallizing the nitroso-thymol, but the crystals of the latter are not so well formed nor as stable as the nitroso-carvacrol.
- 5. In case it is desired to separate the nitroso compounds from quantities of red, oily decomposition products which are frequently encountered in working with these compounds, benzene or a benzene-ether mixture will be found more efficient than either ether or alcohol as recommended in the literature.

Preparation of the Benzoyl Derivatives of Nitroso-thymol and Nitroso-carvacrol.—These compounds have been previously prepared and studied in connection with the structure of the nitroso compounds.

In this study, they were prepared in amounts of 90 g. each, according to the Schotten-Baumann method as outlined by Sherk.²¹ Sherk reports that alcoholysis takes place upon recrystallizing these compounds from alcohol. This can be avoided to a large extent by pulverizing the crude reaction product and thoroughly washing it with a dilute solution of sodium hydroxide and then with water. The compound can be recrystallized from hot alcohol as Sherk describes but a better product can be obtained by recrystallizing the dry compound from hot heptane after removing the water by washing it with alcohol and ether and then drying it in a vacuum. A yield of 92% is easily attainable by this method.

¹⁷ A similar compound has been obtained by Nellie Wakeman in this Laboratory from the hydrolysis of the reaction mixture of piperidine with thymoquinone (unpublished results).

¹⁸ Freudenberg and Peters, Ber., 52, 1463 (1919).

¹⁹ Conant, This Journal, 43, 1705 (1921).

²⁰ Hixon, "Production of Thymoquinone on a Semi-commercial Scale," J. Am. Pharm. Assoc., 11, 696 (1922).

²¹ Sherk, Am. J. Pharm., 93, 207 (1920).

Action of Methylamine upon the Benzoyl-nitroso-phenols.—The study of this reaction was begun at this Laboratory by Miss Julia Whelan.²² It was hoped that amino derivatives might be obtained analogous to the amino-quinones. She reported that a white crystalline compound (m. p., 128–130° with decomposition) was produced by the action of a 33% aqueous solution of methylamine upon a heptane solution of benzoyl-nitroso-thymol. The reaction was also repeated using methylamine hydrochloride with an equivalent of powdered sodium carbonate in dry heptane. Only small quantities of the feathery white crystals could be isolated. The crystals were contaminated with small quantities of darkly colored tar which was believed to be an amino derivative.

In order to push the reaction to completion and also to avoid the presence of water, dry methylamine gas was passed into a solution of benzoyl-nitroso-thymol in dry heptane at 100°. White feathery crystals identical with those obtained by Miss Whelan separated almost immediately. It was almost impossible to free these crystals by fractional crystallization from the tar which was also formed in the reaction. By pressing them on a porous plate and then recrystallizing them from a mixture of ether and heptane, chloroform, and benzene, in the order named, the compound was purified and identified as nitrosothymol. The reaction has also been carried out with benzoyl-nitroso-carvacrol and found to yield the nitroso-carvacrol. Yields of 75% of the calculated nitroso-phenol content have been recovered and, since the tar still contained considerable quantities of the compound, there is no doubt that "hydrolysis" is the principal reaction taking place. It has not been possible to identify the other constituents of the tar.

It is to be noted that the reaction takes place in a water-free medium and cannot be considered as "hydrolysis of an ester" as the term is ordinarily used. If the methylamine is considered to add to the carbonyl oxygen of the benzoyl group in analogy with the previous reactions, a simple explanation of the reaction is possible.

$$O = \begin{array}{c} O \\ = N - O \\ C_{0}H_{5} \end{array} \xrightarrow{H_{2}N - CH_{3}} \left(O = \begin{array}{c} H \mid O \\ C_{0}H_{5} \end{array} \right) \xrightarrow{H} CH_{3}$$

$$O = \begin{array}{c} O \mid C - N \\ C_{0}H_{5} \end{array} \xrightarrow{H} CH_{3} \xrightarrow{C} CH_$$

It should be indicated that the imide group I

$$O = \bigvee_{\mathbf{I}} = \mathbf{N} - \bigvee_{\mathbf{II}} = \mathbf{N} O - \bigvee_{\mathbf{II}}$$

²² Whelan, unpublished results from this Laboratory, 1921.

is an extremely strong base, so that rupture at this bond is not to be expected, while the nitroso-phenol group II is only weakly acid and together with the phenyl group might be expected to impose conditions on the carbonyl group analogous to those of the aliphatic aldehydes or ketones having negative groups (such as double bonds) adjacent to the carbonyl group.

Nitric Acid Addition Products of Benzoyl-nitroso-thymol and Benzoyl-nitroso-carvacrol.—Benzoyl-nitroso-thymol and benzoyl-nitroso-carvacrol form unstable salt-like addition products with nitric acid. When the benzoyl derivatives are dropped into concd. nitric acid, these compounds separate; they are then collected on a filter and dried with filter paper.

The addition product of benzoyl-nitroso-thymol and nitric acid melts at 53° and contains at least 3 molecules of nitric acid. In view of the numerous possibilities the formula can be written only as $C_{17}H_{17}NO_2.3HNO_2$.

The analogous addition product of benzoyl-nitroso-carvacrol melts at 65° and contains 2 molecules of nitric acid per molecule of benzoyl-nitroso-carvacrol, and the formula may therefore be written as $(C_{17}H_{17}NO_2).2HNO_3$.

Both of these nitric acid addition products decompose slowly in air, and instantaneously when thrown into water. They are apparently analogous to the unstable nitric acid addition product of fluorenone, $(C_6H_4)_2C=O$ -HNO₃, described by Schmidt and Bauer²³ and also to the addition compound of phenanthraquinone $(C_6H_4)_2(C=O)_2$.HNO₃ described by Kehrmann and Mattison.²⁴ Such products are of interest in connection with the study of the action of nitric acid on thymoquinone²⁵ and also the action of acids in general on the quinones.

Preparation of Thymoquinone-dioxime.—Goldschmidt and Schmid²⁶ were unable to prepare a dioxime of thymoquinone. In 1890, Kehrmann and Messinger²⁷ found that an excess of hydroxylamine hydrochloride acting upon a saturated alcoholic solution of nitroso-thymol under a reflux condenser gave small yields of thymoquinone-dioxime. The yield could be increased slightly by adding sodium carbonate at frequent intervals but never in sufficient quantities to neutralize all of the hydrogen chloride formed in the reaction. This reaction has been repeated several times in this Laboratory but the yield of the dioxime was never greater than 6–10%.

There appears to be no statement in the literature regarding the action of hydroxylamine upon nitroso-carvacrol. Following the directions of Kehrmann and Messinger for the reaction with nitroso-thymol, yields of the dioxime were obtained varying between 60 and 70%. It is very

- 23 Schmidt and Bauer, Ber., 38, 3758 (1905).
- ²⁴ Kehrmann and Mattison, Ber., 35, 343 (1902).
- ²⁵ Hixon, "Action of Nitric Acid on Thymoquinone," unpublished results.
- 26 Goldschmidt and Schmid, Ber., 17, 2060 (1884).
- ²⁷ Kehrmann and Messinger, Ber., 23, 3557 (1890).

interesting to note that the characteristics of the reaction of thymoquinone with hydroxylamine generally ascribed to "steric hindrance," hold also for the reaction of the monoximes with hydroxylamine.

Thymoquinone-dioxime Dibenzoate.—The dibenzoic ester of thymoquinone-dioxime was prepared by the Schotten-Baumann reaction.

The compound is insoluble in alcohol and ether but crystallizes from hot benzene (5 g. requires about 75 cc. of benzene) as colorless needles. The ester is rapidly saponified by alcoholic sodium hydroxide in the cold. The compound discolors when heated to 170° and melts at 199–200°.

The analysis agrees with the values calculated for the thymoquinone-dioxime dibenzoate.

Analyses. Subs., 0.2000: CO₂, 0.5247; H_2O , 0.0910. Calc. for $C_{24}H_{22}O_4N_2$: C, 71.6; H, 5.4. Found: C, 71.55; H, 5.15.

In view of the fact that the production of the ester from the dioxime takes place practically quantitatively, this compound is of value for purposes of identification.

Summary

- 1. It is pointed out that the quinones, being unsaturated cyclic ketones, should be expected to add ammonia (or ammonia derivatives): (a) at the carbonyl group, in analogy with the aldehyde ammonia compounds; (b) at the double bond, in analogy with some of the unsaturated aliphatic acids. Evidence is presented which indicates that both types of reactions take place with the quinones.
- 2. Evidence is presented that the intermediate addition compounds between amines and quinones have structures analogous to that of ammonia salts. Tertiary amines would be expected to form similar addition compounds with the quinones which would not rearrange. Jackson and Clark have reported that dimethyl-aniline yielded colored addition products with all the quinones at their disposal.
- 3. The reaction between dimethyl-aniline and thymoquinone has been studied. An addition compound appears to be formed which rearranges to a purplish tar. This latter reaction product is difficultly hydrolyzed by 50% sulfuric acid, both mono- and dihydroxy-thymoquinone being obtained. This evidence is indicative (but not conclusive) that tertiary amines may react with quinones just as do primary and secondary amines.
- 4. Details are given for the preparation of nitroso-thymol and nitroso-carvacrol in the crystalline state in quantity from the crude amorphous compounds. The crystalline compounds discolor very slowly in direct sunlight, whereas the crude products are quite unstable.
- 5. Benzoyl "nitroso-thymol" and benzoyl "nitroso-carvacrol" are decomposed by dry methylamine in dry heptane. This reaction cannot be considered as "hydrolysis of an ester" as the term is ordinarily applied.

The reaction is easily explained by the assumption of an intermediate addition compound similar to the aldehyde ammonias.

- 6. Unstable nitric acid addition products of benzoyl "nitroso-thymol" and benzoyl "nitroso-carvacrol" are described for the first time.
- 7. Thymoquinone-dioxime can be prepared more conveniently from nitroso-carvacrol than from nitroso-thymol; the former yielding 70% of the calculated quantity of dioxime whereas the latter yields only 10%.
- 8. The dibenzoic ester of thymoquinone-dioxime is described for the first time. The compound is of value for the identification of the dioxime.

 AMES. IOWA

THE SALTS OF MALEIC, FUMARIC AND INACTIVE MALIC ACIDS

By John Morris Weiss and Charles Raymond Downs Received March 27, 1923

In various investigations which had for their purpose the development of analytical methods for mixtures of maleic, fumaric and malic acids, a number of salts of these three acids were prepared and studied. The results are admittedly incomplete and in certain instances the compounds deserve further study. We are presenting here the results obtained, regretting that we did not have the time to study all the compounds thoroughly but hoping that others will do so. We wish to express our thanks to Dr. G. C. Bailey, Dr. H. E. Williams and Dr. Wolesensky for the careful work which they carried on under our direction in preparing and determining the formulas and solubilities of a number of the compounds described, and to Mr. E. C. Buck for the very careful preliminary search of the literature which he made in this connection.

Ammonium Salts

Analysis.—These salts were analyzed by distilling the material with an excess of standard sodium hydroxide solution and collecting the distillate in an excess of standard sulfuric acid. The distillate, titrated back with methyl orange as indicator, gave the ammonia content; and the flask residue, titrated back with phenolphthalein as indicator, gave the acid radical content.

Ammonium Fumarate.—The product was best prepared by treating fumaric acid suspended in water with concd. ammonium hydroxide in slight excess of the calculated amount, concentrating in a vacuum at not over 60°, adding a little ammonium hydroxide to make up for losses in concentration and allowing the substance to crystallize. The crystals were filtered and washed with alcohol.

Analyses. Calc. for $(NH_4)_2C_4H_2O_4$: NH_3 , 22.67; $C_4H_4O_4$, 77.33. Found: NH_3 , 22.55; $C_4H_4O_4$, 77.40.

The aqueous solution of the salt is stable at 60° but when boiled it loses ammonia; 4.5506 g. of salt was dissolved in 200 cc. of water and the solution distilled, the distillate

¹ Keiser and McMaster, Am. Chem. J., 49, 84 (1913).

being collected in standard acid. In 50 minutes 0.08148 g. of ammonia distilled with 150 cc. water, representing 7.9% decomposition. On the addition and distillation of 150 cc. more water, 0.03933 g. of ammonia was volatilized (3.8%). The final limit of this decomposition or the product formed was not determined.

Ammonium Acid Fumarate.²—Fumaric acid was neutralized by two molecules of ammonium hydroxide with litmus as indicator and a second portion of fumaric acid equal to the first added. The mixture was fractionally crystallized into two lots of crystals, each equivalent to slightly more than $^1/_3$ of the whole, the balance in the mother liquor being discarded.

Analyses. Calc. for NH₄C₄H₃O₄: NH₃, 12.78; C₄H₄O₄, 87.21. Found: Fraction 1: NH₃, 11.70; C₄H₄O₄, 87.70; Fraction 2: NH₃, 12.70; C₄H₄O₆, 87.40.

Ammonium Maleate. 1.3—We were not able to obtain crystalline material by the same method as that used for ammonium fumarate. Under ordinary pressure, the solution does not lose ammonia by evaporation. Only a thick sirup results which cannot be crystallized. When the solution is evaporated in a vacuum, the solid obtained is ammonium acid maleate. This salt deserves attention by future investigators.

Ammonium Acid Maleate.3—This salt was obtained by the same method as described under the corresponding fumarate.

Analyses. Calc. for $NH_4C_4H_3O_4$: NH_3 , 12.78; $C_4H_4O_4$, 87.21. Found: NH_3 , 12.72; $C_4H_4O_4$, 87.16.

Sodium Salts

The sodium acid maleate^{3,4}, sodium maleate^{3,4}, sodium acid fumarate⁵ and sodium fumarate^{2,5,6} were prepared by mixing the acids with the proper amounts of sodium hydroxide in water solution, allowing the salt to crystallize and drying it at room temperature.

The data on water of crystallization as given in the literature were confirmed by ignition to sodium carbonate. In the case of the sodium acid fumarate, where there are no data, we found the crystalline material to be anhydrous.

Barium and Strontium Salts

Barium acid maleate,³ barium maleate,³.7,8, barium fumarate² and barium i-malate³,¹0,¹¹ have been described. We did not isolate these but observed that a heavy white precipitate of slight solubility was obtained when a 10% solution of barium chloride was added to a 10% solution of either sodium maleate or fumarate. With sodium i-malate only a slight precipitate was formed.

- ² Rieckher, Ann., 49, 31 (1844).
- ³ Buechner, Ann., 49, 57 (1844).
- 4 Bodewig, Z. Kryst., 5, 558 (1881).
- ⁵ Chandler, This Journal, 30, 694 (1908).
- ⁶ Kannonikov, J. prakt. Chem., [2] 31, 321 (1885).
- ⁷ Kekulé and Strecker, Ann., 223, 170 (1884).
- ⁸ Vorlaender, Ann., 280, 177 (1894).
- 9 Kekulé, Ann., 117, 120 (1861).
- ¹⁰ Buisine, Compt. rend., 106, 1426 (1888).
- 11 Duboux and Cuttat, Helvetica Chim. Acta, 4, 735 (1921).

Strontium acid maleate and strontium maleate³ and strontium i-malate¹¹ have been prepared.

Strontium fumarate² has been described as containing three molecules of water of crystallization.

We prepared this salt by mixing strontium nitrate and sodium fumarate in water solution in equimolecular proportions, filtering off the precipitate and drying at 100° at which temperature it was anhydrous.

Analyses. Calc. for SrC₄H₂O₄: Sr, 43.45; H, 0.99. Found: Sr, 43.25; H, 1.13.

Calcium Salts

The compositions were determined by igniting the salts to calcium oxide.

Calcium Acid Maleate³ was prepared and found to correspond with the formula as given for 5 molecules of water of crystallization. With the neutral salt³ the same coincidence was observed, this salt containing one molecule of water.

Analysis. Calc. for CaC4H2O4.H2O: Ca, 23.25. Found: 23.28.

Calcium Fumarate^{2,7,12} was prepared by precipitating a sodium fumarate solution with calcium chloride, and filtering, washing and air-drying the product. Our material corresponded to the trihydrate described in the literature.

Analyses. Calc. for $CaC_4H_2O_4.3H_2O$: Ca, 19.23; H, 3.84. Found: Ca, 19.47; H, 4.01.

Calcium Acid Fumarate is not described in the literature. When a solution of sodium acid fumarate was mixed with a molecular equivalent of calcium chloride and evaporated, crystals were obtained which were separated and air-dried.

Analysis. Calc. for CaC₈H₆O₈.2H₂O: Ca, 13.06. Found: 13.22.

Calcium Acid i-Malate¹³ is stated to contain one molecule of water of crystallization. Our preparation was made by heating 52.8 g. of i-malic acid with 20 g. of calcium carbonate, filtering the solution, allowing it to crystallize, and separating and air-drying the crystals; yield, 64 g. The substance was found to be the anhydrous salt.

Analysis. Calc. for CaC₈H₁₀O₁₀: Ca, 13.06. Found: 12.85.

Magnesium Salts

Magnesium acid maleate, magnesium maleate, $^{3\cdot14}$ magnesium fumarate² and magnesium i-malate¹¹ have been described. These salts were not prepared but note was made that none of the three acids is precipitated from its sodium salt solutions (10%) by soluble magnesium compounds. In an attempt to produce the i-malate, magnesium oxide was dissolved in i-malic acid. On concentrating the filtered solution a sirup was obtained which did not crystallize but solidified on standing to a hard white mass.

Cobalt Salts

Cohalt Maleate is not described in the literature.

Cobalt was precipitated as carbonate from a solution of its nitrate and the latter filtered, washed and suspended in water. An equivalent quantity of maleic acid was added and the solution filtered and evaporated.

¹² Carius, Ann., 142, 129 (1867).

¹³ Bremer, Ber., 8, 863 (1875).

¹⁴ Walden, Z. physik. Chem., 1, 529 (1887).

Analysis. Calc. for CoC4H2O4.11H2O: Co, 15.90. Found: 15 15.80.

Cobalt Fumarate² is stated to correspond to the formula CoC₄H₂O₄.3H₂O; this we were unable to confirm. Using concentrated solutions of cobalt nitrate and sodium fumarate, a copious, crystalline, pink precipitate was obtained. This was washed and air-dried.

Analyses. Calc. for CoC₄H₂O₄.4H₂O: C, 19.59; H, 4.08; Co, 24.07. Found: C, 20.36; H, 3.86; Co, 23.93.

When the pink compound was dried at 100° it became somewhat bluish from loss of water.

Analysis. Calc. for CoC₄H₂O₄.2H₂O: Co, 28.23. Found: 28.62.

Cobalt *i*-Malate.—This is not described in the literature. It was prepared by treating cobalt carbonate suspended in water with the calculated amount of *i*-malic acid and evaporating the mixture to dryness at 100° . The formula seems to be that of a trihydrate.

Analyses. Calc. for CoC₄H₄O₅.3H₂O: C, 4.08; H, 24.07; Co, 19.59. Found: C, 4.15; H, 23.40; Co, 19.28.

Nickel Salts

The nickel was determined by digesting a sample with concentrated ammonium hydroxide, adding water, a small amount of sodium iodide (0.02–0.05 g.), a few drops of standard silver nitrate solution and an excess of standard sodium cyanide solution. The excess was titrated back with silver nitrate to a slight permanent precipitate.

Nickel Fumarate² is stated to contain 4 molecules of water of crystallization. The salt was prepared by mixing dilute solutions of nickel nitrate and sodium fumarate and concentrating until a green crystalline precipitate was formed, and removing soluble materials by repeated boiling with water.

Analyses. Calc. for NiC₄H₂O₄.4H₂O: Ni, 24.08; calc. for NiC₄H₂O₄.5H₂O: 22.43. Found: 23.42.

If the precipitation of the nickel fumarate is carried on in concentrated solution, a different product seems to be formed.

Analyses. Calc. for NiC₄H₂O₄.5H₂O: C, 18.27; H, 4.56; Ni, 22.43. Found: C, 18.44; H, 4.06; Ni, 22.30.

Nickel Maleate³ resembles the fumarate in general properties but appears to be more soluble. This compound was not analyzed.

Nickel i-Malate is not described in the literature. It is extremely soluble in water and, therefore, cannot be precipitated. If nickel carbonate is dissolved in malic acid a green solution is obtained which on concentration forms a jelly. On long standing at room temperature, the sample lost water and crystals began to appear. This compound was isolated but not analyzed.

Manganous Salts

Manganous Acid Maleate.—This compound has not been previously described; 69.6 g. of maleic acid was dissolved in the minimum amount of water at 30° and to this was added 34.6 g. of manganese carbonate. A solid separated which was dissolved by warming it. As the solution was cooled in ice water, a granular pink precipitate was formed which was filtered, washed, recrystallized from water and dried at room temperature; yield, 32.5 g.

¹⁵ Cobalt was determined by ignition to cobaltous cobaltic oxide, Co₂O₄.

Analyses. Calc. for $MnC_8H_6O_8.4^1/_2H_2O$: C, 25.60; H, 4.20; Mn, 15.02. Found: C, 25.37; H, 3.91; Mn, 15.19.

From examination of the crystals microscopically, it appears that the salt is stable in the air and in a vacuum over sulfuric acid.

Manganous Maleate has not been previously described. It was prepared in the same manner as the acid salt except that twice as much manganese carbonate was used. It appears to be stable at 100°. In dil. water solution it decomposes with the formation of manganese dioxide.

Analyses. Calc. for $MnC_4H_2O_4.3H_2O$: C, 21.53; H, 3.58; Mn, 24.64. Found: C, 21.01; H, 3.31; Mn, 24.48.

Manganous Fumarate² has been stated to have the formula $\rm MnC_4H_2O_4.3H_2O$. Our results did not confirm this. To 11.55 g, of manganese carbonate we added 11.6 g, of fumaric acid. The slight excess of carbonate was filtered off and the filtrate evaporated until a precipitate appeared, at first flocculent and then granular. This was filtered off and dried at room temperature.

Analyses. Calc. for MnC₄H₂O₄: C, 28.41; H, 1.18; Mn, 32.54. Found: C, 27.55; H, 1.42; Mn, 32.02.

Zinc Salts

Zinc was determined by ignition to zinc oxide.

Zinc Acid Maleate16 was not prepared.

Zinc Maleate³ was made by quickly mixing a saturated maleic acid solution with zinc carbonate as a paste in a mortar and filtering before the zinc maleate separated. Zinc maleate formed as a white, granular precipitate which was washed and dried at room temperature.

Analyses. Calc. for $ZnC_4H_2O_4.2H_2O$: C, 22.80; H, 2.78; Zn, 30.42. Found: C, 21.78; H, 2.78; Zn, 30.68.

When a solution of zinc maleate is heated, it decomposes giving a flocculent precipitate.

Zinc Fumarate² has been described in two modifications with 3 and 4 molecules of water, respectively. Our product was made by treating a suspension of fumaric acid with an excess of zinc carbonate in a mortar, filtering the mixture and evaporating the filtrate until crystallization began. Colorless crystals were obtained and dried at room temperature.

Analyses. Calc. for $ZnC_4H_2O_4.5H_2O$: C, 17.81; H, 4.45; Zn, 24.26. Found: C, 17.24; H, 4.25; Zn, 24.42.

Iron Salts

Ferric Maleate³ has been described as an indeterminate smear. On evaporation of a mixture of two molecular equivalents of ferric hydroxide and three molecular equivalents of maleic acid a dark, nearly black, amorphous mass was obtained which was dried at 100°. When analyzed this showed approximately the composition of the dihydrate.

Analyses. Calc. for $Fe_2(C_4H_2O_4)_3.2H_2O$: C, 29.4; H, 2.04; Fe, 22.88. Found: C, 27.34; H, 2.59; Fe, 22.90.

In solution this material seems to be able to hold an excess of ferric hydroxide. Ferric Fumarate² could not be prepared from ferric hydroxide and fumaric acid. Ferric *i*-Malate¹⁷ was not prepared, but considerable work was carried on with

¹⁶ Richter, Z. Chem., 11, 449 (1868).

¹⁷ Pickering, J. Chem. Soc., 103, 1358 (1914).

ferric ammonium *i*-malate. One molecular equivalent of ferric hydroxide (precipitated cold because when precipitated hot it did not dissolve properly) was mixed with a clear solution of 2 molecular equivalents of malic acid and the mixture was heated to 60°. One molecular equivalent of ammonium hydroxide was then added and the mixture heated rapidly to boiling. The work was carried on in semi-darkness as the material is light sensitive. A clear, red-brown solution resulted which was cooled rapidly in an ice-bath. It showed no ferrous iron when tested with ferricyanide solution. The solution was not stable even in the dark, as ferrous iron appeared on standing and gradually increased. When a thick solution was painted on glass and dried in a dark closet at room temperature a solid similar to ferric ammonium citrate was produced which contained no ferrous iron. When it was dried between 30° and 40° some reduction took place.

To compare the sensitivity of ferric ammonium malate and citrate, dilute solutions of each, free from ferrous iron, were placed in sunlight and tested for ferrous iron. After 5 minutes the malate showed a faint test for ferrous iron and after 10 minutes a very positive test, while the citrate was negative at 24 minutes and showed a positive test only after 39 minutes. In the dark at 100° after 5 minutes the malate showed ferrous iron, while after 20 minutes the citrate still tested negatively.

Attempts to produce ferric ammonium maleate or fumarate in the same way were unsuccessful.

Copper Salts

Copper was estimated volumetrically in acetic acid solution by means of sodium iodide and thiosulfate.

Copper Fumarate^{2,12,18} has been described both as a dihydrate and trihydrate. We obtained our material by precipitating fumaric acid with copper sulfate. The pale blue precipitate was washed and dried at 100°.

Analyses. Calc. for $CuC_4H_2O_4.2H_2O$: C, 22.47; H, 2.80; Cu, 29.78. Found: C, 21.70; H, 3.06; Cu, 29.45.

Copper Maleate^{3,18} was prepared by precipitating a solution of equimolecular equivalents of copper sulfate and maleic acid with sodium carbonate. A deep blue crystalline precipitate formed which, as stated by the previous investigators, is the monohydrate.

Analyses. Calc. for $CuC_4H_2O_4.H_2O$: C, 24.54; H, 2.04; Cu, 32.50. Found: C, 24.05; H, 2.39; Cu, 32.22.

Copper *i*-Malate has not been described. When equivalent quantities of copper carbonate and *i*-malic acid solutions are mixed and the mixture is evaporated, a hard vitreous blue mass is formed which after several weeks becomes crystalline. It contains at this stage 25.02% of copper, which indicates a trihydrate (25.49% of copper). On continued exposure, the mass becomes paler blue and shows the presence of 25.70% of copper.

Analyses. Calc. for CuC₄H₄O_{5.2}H₂O: C, 20.72; H, 3.45; Cu, 27.28. Found: C, 20.86; H, 3.16; Cu, 25.70.

This formula is quite doubtful and further work is indicated.

Cadmium Salts

Cadmium salts of maleic and fumaric acids have not been described in the literature. Cadmium was determined by igniting the salt to the oxide, CdO, in a stream of oxygen.

¹⁸ Pickering, J. Chem. Soc., 101, 174 (1912).

Cadmium Fumarate.—Prepared by precipitating sodium fumarate with cadmium chloride in concentrated solutions this forms a copious, finely divided, white precipitate. It was filtered, washed and dried at 100°.

Analyses. Calc. for $CdC_4H_2O_4$: C, 21.20; H, 0.88; Cd, 49.57. Found: C, 21.63; H, 1.18; Cd, 49.29.

Cadmium Maleate.—This was made by mixing equimolecular proportions of cadmium chloride and sodium maleate in solution and evaporating to crystallization. The salt was washed repeatedly with hot water and dried at room temperature.

Analyses. Calc. for $CdC_4H_2O_4.2H_2O$: C, 18.29; H, 2.28; Cd, 42.75. Found: C, 17.76; H, 2.27; Cd, 42.50.

The salt retains sodium chloride tenaciously and needs exhaustive washing to purify it.

Antimony Salts

No literature references were found to these salts and all attempts to form the maleate, fumarate or i-malate by dissolving antimony trioxide in the corresponding acid were unsuccessful. In the case of i-malate, some oxide is dissolved (never more than 21% of that calculated) but apparently an excess of acid is required to prevent hydrolysis so that the salt cannot be isolated. ¹⁹

Sodium Antimonyl *i*-Malate.—Attempts were made to prepare this salt by heating 40 g. of sodium hydroxide, 144 g. of antimony trioxide and 134 g. of *i*-malic acid in water solution under a reflux condenser. After 15 hours, 82.8 g. of antimony trioxide remained undissolved. This was removed, dissolved in potassium acid tartrate and reprecipitated, washed and added again to the mixture. In this way all but 31 g. of the original quantity was finally dissolved and all attempts to increase this failed. The final solution was evaporated to a thick sirup which on seeding solidified to a white, hard mass. It can be powdered, and is apparently stable and very soluble in water. The problem of these complex salts is interesting and deserves further work.

Lead Salts

Lead was determined gravimetrically as the chromate or by titrating excess of dichromate with sodium iodide and thiosulfate.

Lead Fumarate² is stated to occur as the dihydrate. When equimolar quantities of lead nitrate and sodium fumarate were mixed in aqueous solution, fine crystalline flakes were obtained which were filtered and dried at 100°.

Analyses. Calc. for $PbC_4H_2O_4$: C, 14.91; H, 0.62; Pb, 64.48. Found: C, 14.48; H, 0.88; Pb, 64.22.

Lead Maleate^{3,20} is stated to occur as the trihydrate. When we prepared it in a manner similar to that used for the fumarate, we obtained the anhydrous salt.

Analyses. Calc. for $PbC_4H_2O_4$: C, 14.91; H, 0.62; Pb, 64.47. Found: C, 14.94; H, 0.78; Pb, 64.20.

Lead i-Malate21 is the subject of varying opinion, being reported as anhydrous,

¹⁹ Henderson and Barr, J. Chem. Soc., **69**, 1451 (1896). Henderson and Prentice, *ibid.*, **67**, 1030 (1894).

²⁰ Pelouze, Ann., 11, 263 (1834).

²¹ Lloydl, Ann., 192, 80 (1878). Kekulé, Ann., 130, 1 (1864). Pasteur, Ann. chim., [3] 30, 49 (1852). Werigo and Tanatar, Ann., 174, 367 (1874).

with $1^{1}/2$ molecules water and with 3 molecules water. This salt was obtained as a white precipitate by interaction of lead nitrate and sodium *i*-malate in aqueous solution. When heated to 100° it softens to a dough-like mass. Its formula is doubtful but seems to approach the composition PbC₄H₄O₅. $^{1}/_2$ H₂O.

Analyses. Calc. for $PbC_4H_4O_5$, $^{1}/_2H_2O$: C, 13.78; H, 1.43; Pb, 59.48. Found: C, 11.91; H, 1.46; Pb, 59.42.

Silver Salts

Silver was determined as the chloride.

Silver Maleate^{3,7}.—This was formed by precipitating silver nitrate solution with sodium maleate and was obtained as a white precipitate which was dried at 100°.

Analysis. Calc. for Ag₂C₄H₂O₄: Ag, 65.42. Found: 65.44.

The compound deflagrated when heated during combustion (leaving metallic silver) and the carbon and hydrogen results are considered unreliable.

Silver Fumarate.—This compound has not been described. It was prepared in the same way as was the maleate and behaved similarly. Its silver content was 64.90%.

Solubilities

A number of the salts were tested for solubility in water. Samples were placed in 60cc. bottles with distilled water and securely stoppered. They were then held in a thermostat at the required temperature for 24 hours, 25-cc. portions of the clear solutions were withdrawn in a weighing bottle by means of a pipet with cotton filter, weighed, transferred to a platinum

Table I

Solubilities of Fumarates. Maleates and Malates

Compound	Formula	Solu 25°	bilities ir 30°	g, per 16 40°	00 g, of w	ater 100°
Cadmium fumarate	CdC ₄ H ₂ O ₄		0.09			
Cadmium maleate	$CdC_4H_2O_4.2H_2O$		0.66			
Calcium acid fumarate	$Ca(C_4H_3O_4)_2.2H_2O$		5.19			
Calcium fumarate	$CaC_4H_2O_4.3H_2O$		1.56			
Calcium acid maleate	$Ca(C_4H_3O_4)_2.5H_2O$	21.13		41.89	94.78	
Calcium maleate	CaC ₄ H ₂ O ₄ .H ₂ O	2.49		2.88		
Cobalt fumarate	$C_0C_4H_2O_4.4H_2O$		0.88			
Copper fumarate	$CuC_4H_2O_4.2H_2O$		0.02			
Copper maleate	$CuC_4H_2O_4.H_2O$		0.12			
Lead fumarate	$PbC_4H_2O_4$		0.025			
Lead i-malate	$PbC_4H_4O_5.1/_2H_2O$	• • •	0.21			
Lead maleate	$PbC_4H_2O_4$		0.052			
Manganous fumarate	$MnC_4H_2O_4$		0.14			
Nickel fumarate	$NiC_4H_2O_4.5H_2O$		0.36			
Silver fumarate	$AgC_4H_2O_4$		0.013			
Silver maleate	$AgC_4H_2O_4$		0.12			
Sodium acid fumarate	$NaC_4H_3O_4$	6.87		10.74	18.15	30.2
Sodium fumarate	Na ₂ C ₄ H ₂ O ₄	22.83				
Sodium acid maleate	$NaC_4H_3O_4.3H_2O$	6.73		12.81	31.3	288.0
Sodium maleate	Na ₂ C ₄ H ₂ O ₄ . ¹ / ₂ H ₂ O	96.06				
Strontium fumarate	SrC ₄ H ₂ O ₄	• • •	0.29		of the s	
Zinc fumarate	ZnC ₄ H ₂ O ₄ .5H ₂ O		1.96			
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dish, evaporated to dryness and heated to constant weight at 100°. With the acid salts, the amount of solute was determined by titration. The sampling of the solutions saturated at 60° and 100° was done entirely under the surface of the water in the thermostat with an apparatus described by Pawlewski.²²

The solubility results are given in Table I.

Summary

The data in the literature regarding the salts of maleic, fumaric and *i*-malic acids have been reviewed and the water of crystallization of a number of these salts determined. In some cases the work agrees with that of past observers, but in others new numbers are apparently justified. Some 11 salts, not previously described, were prepared and the water of crystallization determined in certain cases definitely.

The solubilities in water of 22 salts were determined and tabulated. In general, fumarates are less soluble than the corresponding maleates.

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[CONTRIBUTION FROM THE STEELE CHEMICAL LABORATORY, DARTMOUTH COLLEGE]

THE REACTION OF CARBON DISULFIDE ON PARA-PHENYLENEDIAMINE

By C. Ernest Bolser and Elden B. Hartshorn Received March 31, 1923

In the description of a patented process¹ for making symmetrical p-diamino-diphenyl-thio-urea, the statement is made that when carbon disulfide reacts on p-phenylenediamine in alcoholic solution two compounds are formed, symmetrical p-diamino-diphenyl-thio-urea, I, and phenylenethio-urea, a compound insoluble in cold, dil. acids and all ordinary solvents. This compound was originally described by Lellmann² and given Formula II.

$$H_2N$$
 $C=S$
 H_2N
 H
 H
 H
 H
 H
 H

The description of the patented reaction is meager, and the formation by primary reaction of two substances to one of which is assigned Formula

- ²² Pawlewski, Ber., 32, 1040 (1899).
- ¹ Wm. Noetzel and Co., Ber., 24, 849 (1891).
- ² Lellmann, Ann., 221, 29 (1883). Gucci, J. Chem. Soc. Abs., 64, 588 (1893).

II is illogical. Formula II, also, is not in accord with the probable structure of most para ring compounds. This paper, then, is a contribution to the study of para ring compounds which have been the subject of several investigations including those of von Braun,³ Perkin and Titley,⁴ and Adams and Wilson.⁵

In carrying out the patented reaction it was found that when the usual procedure of prolonged boiling in alcoholic solution was followed, a very small percentage of the reaction product consisted of the diamino-thiourea, I. To avoid the formation of the insoluble compound, p-amino-acetanilide was substituted for p-phenylenediamine, the intention being to mask one of the amino groups during the reaction with carbon disulfide, and to restore this group later by hydrolysis of the reaction product. The acetyl derivative of the diamino-diphenyl-thio-urea, (CH₃CO.NH.-C₆H₄NH)₂CS, formed readily, but all attempts to hydrolyze this compound resulted in its decomposition with the formation of phenylenediamine.

After several unsuccessful attempts to overcome the difficulty by the preparation of diazobenzene-p-thio-urea, and some of its derivatives, and their subsequent reduction, a more complete study of the patented reaction was made. This revealed that the yield of diamino-diphenylthio-urea could be increased by causing the reaction to proceed at a lower temperature with a reduced concentration of carbon disulfide, and the frequent removal of the reaction product by filtration. These experimental conditions indicated that success depended upon the removal by filtration of the diamino-diphenyl-thio-urea, which, due to its relatively slight solubility in alcohol at the lower temperature, crystallized from the solution when the proper concentration was attained. This in turn suggested that the insoluble product was not the result of primary reaction of carbon disulfide on phenylenediamine, but was due rather to secondary reaction, and that its formation would be prevented in proportion to the completeness of the removal of the primary product, I.

To accomplish this result, water in which diamino-diphenyl-thio-urea is much less soluble was substituted for alcohol as a solvent, and a special apparatus was devised to keep the temperature as near the boiling point of carbon disulfide as possible, and the concentration of the latter low. This procedure resulted in suppressing the formation of the insoluble material almost entirely. The next step was obviously to bring diamino-diphenyl-thio-urea into reaction with carbon disulfide in alcoholic solution. As expected, an insoluble compound was formed in approximately the amount demanded by the only logical formulation of the reaction, namely, $(H_2NC_6H_4NH)_2CS + CS_2 = SC(HNC_6H_4NH)_2CS + H_2S$.

³ von Braun, Ber., 45, 1274, 2512 (1912), and later articles.

⁴ Perkin and Titley, J. Chem. Soc., 122, 1562 (1922).

⁵ Adams and Wilson, This Journal, 45, 528 (1923).

Final proof that the reaction of carbon disulfide on phenylenediamine proceeds in two stages would, of course, demand that the identity of the insoluble compound formed directly from phenylenediamine with that formed from diamino-diphenyl-thio-urea be established. By neither reaction was it possible to obtain a pure product. This is apparently due to occlusion of impurities from which the product, on account of its insolubility, cannot be freed by crystallization. Both products decompose above 285°. When heated with strong acids, they dissolve with the formation of phenylenediamine. Fortunately, they are decomposed, although extremely slowly, by boiling acetic anhydride with the formation of pphenylene-diisothiocyanate, SCNC₆H₄NCS. This substance was obtained in small quantity, and was identified by its crystal form, its melting point (130°) and by the fact that a dithio-urethane of the proper melting point (197°) and crystal form was obtained from it. Not only does this reaction prove that the compounds in question are identical, but it furnishes further proof of their constitution. The formula of the substance must be

and the reaction formulated as follows: $SC(HNC_6H_4NH)_2CS + (CH_3CO)_2O = SCNC_6H_4NCS + (CH_3CONH)_2C_6H_4 + 2CH_3COOH$; for with Formula II the dimustard oil could not be formed, but should give the acetyl derivative of *p*-aminophenyl-isothiocyanate. Since this acetyl derivative is unknown, we prepared it. It crystallizes in needles melting at 195°. We were unable to discover any of it in the reaction product.

Complex thio-ureas of a higher molecular weight than that of p-diphenylene-dithio-urea were formed only by the reaction of carbon disulfide on diamino-thio-ureas having a higher molecular weight than p-diamino-diphenyl-thio-urea, I. Theoretically, such compounds might form. The homogeneity of the diamino-thio-urea formed, as shown by its crystal form, constant melting point after repeated crystallizations, and the analysis of its sulfate, seems to preclude this possibility.

In the various attempts to hydrolyze acetyl-aminophenyl-isothiocyanate referred to above, small amounts of a substance insoluble in hydrochloric acid had been obtained which, in the light of facts already discussed, led us to believe that p-aminophenyl-isothiocyanate had been formed, and that two molecules of this had then reacted to form p-diphenylene-

dithio-urea, III, whose constitution has just been established. However, it would seem logical that if the simple thio-urea, II, had any tendency to form under any conditions it would do so here where an intramolecular change alone is involved. It seemed highly desirable, therefore, to find some reaction by which p-aminophenyl-mustard oil would be formed and not further decomposed, in order that its behavior might be studied. Now, when diamino-diphenyl-thio-urea is boiled with glacial acetic acid a white insoluble powder results which yields phenylene-dimustard oil on treatment with acetic anhydride and is, therefore, p-diphenylenedithio-urea. The amount formed is approximately that demanded by the equation: $2(H_2NC_6H_4NH)_2CS + 4CH_3COOH = SC(HNC_6H_4NH)_2$ $CS + 2C_6H_4(NH_2)_2$. 2CH₃COOH. When the reaction mixture is diluted with water and filtered, the mother liquor deposits slowly an additional quantity of the same substance. When this mother liquor is rendered alkaline an immediate precipitate of the same substance results. These facts show clearly that the p-aminophenyl-mustard oil is first formed but that even in acetic acid solution the major portion condenses to form diphenylene-dithio-urea. They show further that the free base cannot exist, in solution at least, but that it immediately forms the complex thio-urea.

To bring out this point still more conclusively we prepared azobenzene p-isothiocyanate by the reaction of thiophosgene on p-amino-azobenzene and reduced this compound in acetic acid solution with stannous chloride and hydrochloric acid. Under these experimental conditions, lower temperature and presence of hydrochloric acid, the mustard oil formed does not immediately form the thio-urea, as was the case at the boiling point of acetic acid, but as soon as the clear acid solution was made sufficiently alkaline to dissolve the tin hydroxides and free the base, the insoluble high-melting diphenylene-dithio-urea appeared. Here again, as under the other conditions cited, the more complex rather than the simpler compound forms.

The simpler compound is supposed to have been obtained² by heating phenylene-diphenyl-dithio-urea, the addition product of two molecules of aniline and one of phenylene-diisothiocyanate, to high temperature. It is well known that under these conditions intermolecular changes readily take place. In the light of these facts, the demonstrated stability of the dimolecular compound and its tendency to form, where the formation of the simpler substance might be expected, throws a reasonable doubt on the existence of the latter compound.

We are now extending this method of investigation to other diamines, especially to o- and m-phenylenediamine and to benzidine.

Experimental Part

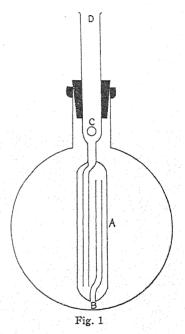
Reaction of Carbon Disulfide on p-Phenylenediamine in Alcoholic Solution.— Ten g. of phenylenediamine was dissolved in 250 cc. of alcohol and boiled on a steam-bath with an excess of carbon disulfide for 10 hours. The reaction mixture was filtered and the residue extracted with cold, dil. hydrochloric acid. By making the extract alkaline, $0.45\,\mathrm{g}$. of diamino-diphenyl-thio-urea was obtained. The insoluble residue was boiled with alcohol, then with water, and finally dried; yield, about 10 g. In a melting-point tube the substance commences to darken at about 200° and rapid decomposition takes place above 280°.

Reaction of Carbon Disulfide with p-Phenylenediamine in Aqueous Solution.—A solution of 10 g. of phenylenediamine in 250 cc. of water was placed in a round-bottomed flask to which was fitted the apparatus shown in Fig. 1. The tube A, connected with a reflux condenser at D, contained about 5 cc. of carbon disulfide and when the flask was heated on the steam-bath to the proper temperature, the vapor of carbon disulfide escaped through Tube B into the reaction mixture. The excess of vapor entered

the condenser through the opening C and the condensed liquid was returned to Tube A. During the reaction, which was allowed to continue for 10 hours, a precipitate gradually formed. This was filtered out, washed with alcohol, and extracted with dil. hydrochloric acid at room temperature. All but a small amount (about 0.8 g.) dissolved immediately and the residue was allowed to stand in the acid overnight. The solution was then filtered from the insoluble residue and made alkaline. A voluminous crystalline, nearly white precipitate was obtained, which was crystallized from boiling water-about 2 liters were requiredfiltered and dried. The compound separates in plates melting at 194-195°; yield, 8.95 g.; calculated yield, 11.94 g. The normal sulfate was prepared by precipitation.

Analysis. Subs., 0.3025: BaSO₄, 0.1958. Calc. for $C_{13}H_{14}N_4S.H_2SO_4$: SO₃, 22.47. Found: 22.20.

Reaction of Carbon Disulfide with Diaminodiphenyl-thio-urea.—Five g. of diamino-diphenylthio-urea was dissolved in 200 cc. of alcohol and the solution boiled with a large excess of carbon disulfide under a reflux condenser for 12 hours. The



clear solution soon became clouded with a precipitate which gradually increased in amount. The separated reaction product was treated successively with cold, dil. hydrochloric acid, boiling alcohol, and boiling water, and finally dried; yield, 5.55 g.; calculated yield, 5.81 g. This compound behaved in a melting-point tube exactly like the insoluble substance described above.

Proof of the Composition of the Insoluble Substances thus Obtained.—Lots of 7 g. of each of the insoluble compounds obtained by the reactions described above were boiled in separate flasks with 15 cc. of acetic anhydride for half an hour. Apparently, very little of the substance had gone into solution, but for fear of decomposition of the reaction product, the operation was interrupted and the reaction mixture filtered into water. This was then repeated several times with each residue. The combined filtrates in each case were warmed to decompose excess of acetic anhydride and a crystalline solid

Werner, J. Chem. Soc., 59, 396 (1891).

remained. By repeated recrystallization of this solid from glacial acetic acid there was obtained from each of the insoluble substances in question approximately 0.1 g. of a white compound crystallizing in long, shiny needles; m. p., 130°. Heated on the steambath with ethyl alcohol for 8 hours, this compound yielded a white crystalline powder melting at 197°. These crystal forms and melting points identify these compounds as phenylene-diisothiocyanate and the corresponding p-thio-urethane. These substances are then identical and are diphenylene-dithio-urea, III.

Reaction of Glacial Acetic Acid on Diamino-diphenyl-thio-urea.—Three g. of diamino-diphenyl-thio-urea was heated to boiling with 15 cc. of glacial acetic acid. Complete solution took place as the mixture was warmed. At the boiling point a finely divided substance began to separate, and in two or three minutes it was so abundant that the reaction mixture was nearly white. The boiling was continued for 10 minutes, when the product was poured into water. From the finely divided white powder obtained by filtration no unchanged diamino-diphenyl-thio-urea could be obtained by extraction with dil. hydrochloric acid. This powder was boiled with alcohol, then with water, and dried; yield, 1.60 g.; calculated yield, 1.92 g. In a melting-point tube it behaved like the diphenylene-dithio-urea identified as described above.

Analysis. Subs., 0.1516: N, 25.8 cc. (22°, 754.4 mm.). Calc. for $C_{14}H_{12}N_4S_2$: N. 18.66. Found: 19.06.

By treatment with acetic anhydride, phenylene-p-diisothiocyanate was obtained from this substance, and its identity with diphenylene-dithio-urea thus further established.

p-Diacetylamino-diphenyl-thio-urea, (CH₃COHNC₆H₄NH)₂CS.—Ten g. of p-amino-acetanilide was dissolved in 400 cc. of alcohol and the solution was heated in a water-bath under a reflux condenser with an excess of carbon disulfide for about 10 hours. A white, insoluble precipitate was formed, which in the agitated mother liquor somewhat resembled long-fibered asbestos. After it was filtered, washed and dried, 10.2 g. of pure, white solid was obtained that was insoluble in all ordinary solvents; m. p., 235–237°.

This compound could not be hydrolyzed except by boiling with strong acids. Under these conditions the expected diamino-diphenyl-thio-urea decomposed with formation of phenylenediamine which was identified by Lauth's violet test.

Analysis.³ Subs., 0.1896: N, 27.90 cc. (18.8°, 736 mm.). Calc. for $C_{17}H_{18}N_4O_2S$: N, 16.3. Found: 16.4.

p-Acetylamino-phenyl-isothiocyanate, CH₃CONHC₆H₄NCS.—Ten g. of the thiourea described above was boiled in an oil-bath with 30 g. of acetic anhydride. Solution took place in about 10 minutes, whereupon 200 cc. of water was immediately added. After the mixture had cooled, the precipitated solid was crystallized from alcohol as white needles; m. p., 195–196°; yield, 4.1 g. Care had to be taken not to heat it long enough with the alcohol to cause the formation of the thio-urethane.

Analysis. Subs., 0.2285: N, 29.4 cc. over 30% KOH (21.5°, 756 mm.). Subs., 0.1916: BaSO₄, 0.2304. Calc. for $C_9H_8ON_2S$: N, 15.58; S, 16.66. Found: N, 14.53; S, 16.51.

Hydrolysis of p-Acetyl-amino-phenyl-isothiocyanate.—Two g. of this compound was suspended in 30 cc. of coned. hydrochloric acid and the mixture was heated on the water-bath. Solution took place with foaming and white plates of phenylenediamine hydrochloride separated. Upon the addition of coned. hydrochloric acid a further sepa-

⁷ Billeter and Steiner, Ber., 20, 230 (1887).

⁸ This analysis was made by Mr. G. W. Anderson.

⁹ This analysis was made by Mr. F. W. Vogel.

ration took place. This precipitate (0.9 g.) was then filtered, washed, dried over potassium hydroxide and analyzed.

Analysis. Subs., 0.3012: AgCl, 0.4736. Calc. for $C_6H_{10}N_2Cl_2$: Cl, 39.18. Found: 38.90.

Azobenzene-p-isothiocyanate, $C_6H_5NNC_6H_4NCS$.—Fifteen g. of p-amino-azobenzene and the same weight of thiophosgene were heated in 400 cc. of carbon tetrachloride for 4 hours on a boiling water-bath. The solution was filtered from amino-azobenzene hydrochloride and the filtrate allowed to evaporate spontaneously. The residue was crystallized from 80% acetic acid, forming salmon-colored needles; m. p., 94–95°; yield, 8.4 g.

Analyses. Subs., 0.2003: CO₂, 0.4778; H₂O, 0.0713. Subs., 0.1556: BaSO₄, (Carius) 0.1526. Calc. for $C_{12}H_9N_3S$: C, 65.22; H, 3.79; S, 13.41. Found: C, 65.06; H, 3.98; S, 13.47.

Reduction of Azobenzene-p-isothiocyanate.—When 2 g. of this substance was dissolved in 300 cc. of glacial acetic acid and 12 g. of stannous chloride in a small quantity of hot coned. hydrochloric acid was added, the orange color of the solution almost entirely disappeared. Upon dilution and the addition of enough coned. sodium hydroxide solution to redissolve the precipitated tin hydroxides, a finely divided powder separated. This powder was insoluble in dil. hydrochloric acid and in boiling 80% acetic acid and resembled completely the diphenylene-dithio-urea obtained by other reactions described above, except for a slight greenish tinge.

Summary

- 1. The reaction of carbon disulfide on p-phenylenediamine proceeds in two stages. In the first p,p'-diamino-diphenyl-thio-urea is formed, and in the second this is changed into diphenylene-dithio-urea. There is no evidence of the formation of phenylene-thio-urea, which was thought to be a product of the primary reaction of carbon disulfide on p-phenylene-diamine.
- 2. p-Aminophenyl-isothiocyanate cannot exist in the free state in solution. It changes immediately into the complex dithio-urea. This reaction also takes place in boiling acetic acid, and slowly in dil. acetic acid at room temperature. There is no evidence of the formation of phenylene-thio-urea under these conditions.
- 3. Reasonable doubt has been thrown on the existence of phenylene-thio-urea.
- 4. These results are in agreement with the probable constitution of most para ring compounds.

HANOVER, NEW HAMPSHIRE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE BENZIL REARRANGEMENT. V. CANNIZZARO'S REACTION

By ARTHUR LACHMAN RECEIVED APRIL 25, 1923

In several recent papers¹ it has been shown that rearrangements of the benzil and pinacol types are essentially questions of intramolecular oxidation and reduction. The present paper deals with Cannizzaro's reaction.

Introduction

As Cannizzaro² discovered, benzaldehyde rapidly solidifies when shaken with an excess of a strong solution of sodium hydroxide. Much heat is developed. The reaction mass contains nearly equal molecular equivalents of sodium benzoate and of benzyl alcohol; little or no unchanged benzaldehyde is recovered.

 $2C_6H_5-CHO + NaOH = C_6H_5-COONa + C_6H_5-CH_2OH$ (1) This is a typical oxidation-reduction process.

A number of observers have found that if water is excluded in this reaction, benzyl benzoate is a primary product. Claisen³ added sodium methoxide to benzaldehyde, and obtained a mixture of benzyl benzoate and methyl benzoate; and he found that a small amount of sodium benzoxide was capable of converting a large quantity of benzaldehyde directly into benzyl benzoate. Kohn and Tranton⁴ heated benzaldehyde with solid sodium hydroxide, in benzene suspension, and were able to isolate some benzyl benzoate from the mixture Tischtschenko⁵ obtained esters of benzoic acid when he treated benzaldehyde with aluminum alcoholates.

Action of Aqueous Alkali on Benzaldehyde

Benzyl benzoate is formed, however, even in the presence of water, if precautions are taken to prevent its subsequent hydrolysis. These precautions involve merely avoidance of an excess of alkali, and prevention of any considerable rise in temperature. In the following table are given some of the results obtained.

In each case, 106 g. of benzaldehyde was shaken in a tightly stoppered flask, with sodium hydroxide solution. After a few minutes, when emulsification had taken place, the mixture was stood in cold water for the periods noted. To isolate benzyl benzoate, the mass was covered with ether, and sufficient cold water added, with stirring, until complete solu-

- ¹ Lachman, This Journal, 44, 330 (1922); 45, 1509, 1522, 1529 (1923).
- ² Cannizzaro, Ann., 88, 129 (1853).
- ³ Claisen, Ber., 20, 646 (1887).
- ⁴ Kohn and Tranton, J. Chem. Soc., 75, 1155 (1899).
- ⁵ Tischtschenko, Chem. Centr., [II] 77, 1309, 1552 (1906).

tion occurred. The ether solution was separated, filtered, evaporated and the ether distilled at atmospheric pressure until the vapor temperature reached 220°; the residue was finally distilled at 15 mm. pressure until the temperature of the vapors reached 200°. There was usually a small amount of still higher-boiling residue. From the alkaline solution, benzoic acid was precipitated and weighed. The amount of benzyl alcohol produced, and of unchanged aldehyde recovered, was not estimated. The yields varied irregularly, as must be expected on account of the uncontrolled heating at the start. When 10 N alkali is used, the emulsion is very thin, and does not thicken much as reaction proceeds; and the rate is very slow. With a concentration of $14\,N$ or over, a very thick emulsion forms rapidly, which sets to a hard cake in a short time, and must be cooled promptly to prevent complete hydrolysis of the ester.

NaOH added Mol. eq.	Time Hours	Benzyl benzoate G.	Benzoic acid G.		NaOH added Mol. eq.	Time Hours	Benzyl benzoate G.	Benzoic acid G.	
NaOH concentration 10 N				NaOH concentration 14 N					
0.5	2	• •	2		0.5	4	5	27	
.5	2	1	1		.5	48	3	35	
.5	18	9	8		.25	48	7	16	
.5	24	3	7		.10	48	4	6	
.5	48	8	5		NaC	Н сопсе	ntration .	19 N	
.5	48	6	9		.5	24	9	51	
.5	72	7	8		.25	24	12	28	
.5	96	5	18		.10	18	10	8	
.25	48	5	8		.10	24	8	12	
••			••.		.10	72	9	13	

The benzyl benzoate obtained above is not entirely pure. 1.40 g., boiled with dil. sodium hydroxide, used up 5.9 cc. of N solution, gave 0.72 g. of benzoic acid, melting at 121.5°; ester content, 89%. A number of samples, combined and carefully refractioned at 5 mm., gave considerable dibenzyl ether, boiling at 130–135°, in addition to the main fraction at 150–155°, which was practically pure benzyl benzoate; there was also a small amount of a high-boiling product. The origin of dibenzyl ether is discussed below.

It is interesting to note that in several instances mentioned above, nearly half of the total amount of benzoic acid produced could be isolated in the form of the ester. The failure of the reaction to proceed to completion, especially when $10\,N$ alkali was used, is probably entirely a matter of solubility relations, and not of alkali concentration; $106\,\mathrm{g}$. of benzaldehyde was dissolved in $150\,\mathrm{cc}$. of methyl alcohol, and $0.5\,\mathrm{equivalent}$ of sodium hydroxide dissolved in $50\,\mathrm{cc}$. of water was added. The alkali was therefore $2.50\,N$, only $^1/_4$ of the lowest concentration used above. The perfectly homogeneous liquid began to warm up almost immediately; it was placed in cold water, and soon solidified. After $24\,\mathrm{hours}$, $46\,\mathrm{g}$. of benzoic acid and $6\,\mathrm{g}$. of benzyl benzoate were obtained.

Dibenzyl Ether

Dibenzyl ether was first obtained by Cannizzaro, upon heating benzyl alcohol with boric anhydride. Later, Lowe prepared the ether by the action of benzyl chloride on sodium benzoxide. A few years ago, Meisenheimer showed that considerable quantities of dibenzyl ether appear when benzyl alcohol is prepared from benzaldehyde, and he traced its formation to the use of sodium bisulfite to remove unchanged aldehyde. Small amounts of sulfurous acid are retained in the benzyl alcohol, and during its distillation catalytically convert the alcohol into its ether.

During the course of the present work, it has been found that alkalies also convert benzyl alcohol into its ether; $50~\rm g$. of benzyl alcohol, freshly distilled in a vacuum, was warmed on the water-bath for 4 hours with $25~\rm cc.$ of 10~N sodium hydroxide; $0.9~\rm g.$ of dibenzyl ether was obtained. The same quantities, boiled for 2 hours, gave $0.8~\rm g.$

In fact, the dehydration of benzyl alcohol may take place without any catalyst at all, other than the glass vessel in which it is heated; 30 g. of freshly rectified benzyl alcohol was heated in a sealed tube to 210–215° (b. p., 207°) for 5 days. No pressure was observed when the tube was opened. Water had visibly separated; on distilling the mixture, the products obtained were 2.0 g. of water, 6.0 g. of unchanged benzyl alcohol, 3.0 g. of dibenzyl ether, and 17 g. of other substances which came from a decomposition of most of the dibenzyl ether that had formed, namely, 6.9 g. of toluene, 6.1 g. of benzaldehyde, 3.8 g. of high-boiling residue.

The heat decomposition of dibenzyl ether, just referred to, was discovered by Cannizzaro. Lowe repeated the observation; and a brief study was published by Oddo. Lowe gives the decomposition temperature as at or above the boiling point, 295–298°. The reaction occurs, however, at a much lower temperature; 30 g., freshly distilled in a vacuum, was heated for 5 days, in a sealed tube, to 210–215°. No gas was formed; the products were 8.5 g. of toluene, 7.5 g. of benzaldehyde, 8 g. of unchanged ether and 5.5 g. of high-boiling residue. No trace of water was found. The main reaction thus corresponds to the equation

$$C_6H_5-CH_2-O-CH_2C_6H_5 = C_6H_5-CH_3 + C_6H_5CHO$$
 (2)

The bulk of the high-boiling residue is formed from dibenzyl ether and not by condensation of benzaldehyde; the molecular ratio of toluene and of benzaldehyde isolated is 1:0.8. The high-boiling residue is a complex mixture; the chief component is an oil, boiling constant at 217° (5 mm.).

The pyrolytic decomposition of dibenzyl ether is evidently also a matter of intramolecular oxidation and reduction. The reaction sheds light

⁶ Cannizzaro, Ann., 92, 113 (1854).

⁷ Lowe, Ann., 241, 374 (1887).

⁸ Meisenheimer, Ber., 41, 1420 (1908).

⁹ Oddo, Gazz. chim. ital., 31, I, 367 (1901).

on some obscure phenomena. O. and W. F. Kamm¹⁰ have recently discussed the appearance of dibenzyl ether during the preparation of benzyl benzoate. They suggest that the addition product of benzyl benzoate and of sodium benzoxide decomposes as follows,

 $C_6H_5-C(ONa)(OCH_2C_6H_5)_2=C_6H_5-COONa+(C_6H_5-CH_2)_2O$ (3) But benzyl alcohol, when heated with sodium benzoxide, also yields sodium benzoate and dibenzyl ether; 2 g. of sodium was dissolved in 30 cc. of benzyl alcohol, and the mixture heated to 190° for one hour, in a long, open tube. After cooling the reaction mixture and adding water to it, the alkaline liquid gave 1.4 g. of benzoic acid; and the alcohol contained 2.5 g. of dibenzyl ether. As it was possible that benzoic acid owed its production to atmospheric oxygen, the experiment was repeated; the tube was drawn out before the sodium was dissolved, and sealed immediately afterwards. After heating to only 150° for 45 hours, 0.9 g. of benzoic acid, 1.4 g. of dibenzyl ether, and 1.2 cc. of toluene were isolated. No gaseous products were noted.

It is clear that when benzyl alcohol is heated with sodium benzoxide, dibenzyl ether is formed.

 $C_6H_5CH_2OH + C_6H_5CH_2ONa = C_6H_5CH_2-O-CH_2C_6H_6 + NaOH$ (4) The ether undergoes metakliny (oxidation-reduction) as in Equation 2, forming toluene and benzaldehyde; and the latter finally goes over into benzoic acid according to the reaction known by Cannizzaro's name

(Equation 1).11

Perfumers who use benzyl alcohol have trouble in freeing it from dibenzyl ether and above all, from benzaldehyde.¹² The changes described above must go on slowly at ordinary temperatures, and it is more than likely that they are catalyzed by light. Benzyl alcohol distilled at atmospheric pressure will always contain notable traces of both impurities.

The Action of Bromine on Dibenzyl Ether

A measured amount of bromine was slowly dropped into 48 g. of dibenzyl ether. Each addition caused a rapid rise in temperature, and hy-

10 O. and W. F. Kamm, "Organic Synthesis," John Wiley and Son, N. Y., 1922, p. 60.

¹¹ When a mixture of sodium and amyl alcohol is used for reduction, large quantities of valeric acid appear. In order to see whether the mechanism of this reaction is the same as that just described, 1.8 g. of sodium was dissolved in 20 g. of amyl alcohol, and the solution heated in a sealed tube for 24 hours, the temperature gradually rising to 220°. The tube contained hydrogen at very high pressure. After water had been added, the alcohol layer was distilled. The first drop passed over at 92° and all distilled below 135°. Valeraldehyde boils at 93°, amyl ether at 176°. From the first portion of the distillate, phenylhydrazine formed 1.2 g. of hydrazone, equivalent to 0.6 g. of valeraldehyde. The water layer yielded 2.6 g. of valeric acid. Amyl alcohol does not form its ether under the conditions described, but loses hydrogen directly to give the aldehyde: C₄H₂CH₂OH = C₄H₂CHO + H₂.

¹² Compare G. Blanc, C. A., 16, 3308 (1922).

drogen bromide soon passed off. The mixture, which was dark red, was maintained at from 70–100° by its own reaction heat. No bromine fumes were visible above the liquid until 80 g. had been added. The mixture was then slowly distilled; 72 g. passed over below 230°. This colorless liquid, which fumed strongly, was allowed to stand overnight with an excess of sodium carbonate solution; it was then refluxed for 1 hour, cooled, and separated. The oily layer was distilled, passing over completely between 196° and 202°; it was practically pure benzyl bromide, and weighed 32 g. The sodium carbonate solution, when acidified, gave 36 g. of benzoic acid.

The action of bromine on dibenzyl ether is given by the equation

$$C_6H_5CH_2 - O - CH_2C_6H_5 + 2Br_2 = C_6H_5CH_2Br + C_6H_5 - CO - Br + 2HBr \eqno(5)$$

The formation of benzoyl bromide was shown in a separate experiment in which the first distillate was directly treated with alcohol; a large amount of ethyl benzoate was formed, but its separation from benzyl bromide, with nearly the same boiling point, proved difficult. The isolated reaction products, in the experiment detailed above, correspond to a recovery of 80%.

The action of bromine on dibenzyl ether is very similar to that of temperature increase; in both cases metakliny occurs. The yields also correspond closely; making allowance for recovered dibenzyl ether, the amount of toluene found above is 87% of that called for by Equation 2.

The Addition of Benzoyl Bromide to Benzaldehyde

In connection with the present investigation, the substance known as bromobenzyl benzoate was examined. This substance is formed by the addition of benzoyl bromide to benzaldehyde.¹³ Action takes place spontaneously, with development of a little heat; when distilled, the substance passes over at about 200°, with complete dissociation into its components, which reunite slowly on cooling.

The reaction is considered to take place as follows:

$$C_{6}H_{5}-CO-Br + C_{6}H_{5}-CHO = C_{6}H_{5}CO-O-CHBrC_{6}H_{5}$$
 (6)

The present inquiry was directed towards the nature of the linking,—whether the central carbon atoms are tied to oxygen, as shown, or whether perhaps they are directly united. In the latter case, the substance would be related to benzil or benzoin, and most likely have the structure of benzil hydrobromide, $C_6H_5-CO-C(OH)(Br)C_6H_5$.

No such substance could be prepared by melting benzil and passing dry hydrogen bromide over it; no action of any kind took place.

Forty-five g. of crystalline bromobenzyl benzoate was covered with 50 cc. of absolute alcohol, and allowed to stand in a vessel surrounded by cold water until complete solution occurred. Then a slight excess of sodium

¹³ Liebig and Wohler, Ann., 3, 266 (1832). Laurent and Gerhardt, Jahresber., 1850, 489. Schiff, Ann., 154, 347 (1870). Claisen, Ber., 14, 2475 (1881).

carbonate solution was slowly added, and the mixture distilled at low pressure until most of the alcohol passed over. This contained a small amount of ethyl bromide which was not estimated. After extraction with ether and evaporation of the solvent, an oil was obtained which upon distillation gave 15.9 g. of benzaldehyde, and 8.8 g. of ethyl benzoate; no benzil, benzoin, or other high-boiling residue could be noted. From the sodium carbonate solution 11.8 g. of benzoic acid was recovered.

From these results, bromobenzyl benzoate must be regarded as a compound with oxygen linking, as indicated by its name.

The Mechanism of Cannizzaro's Reaction

The data in the present paper afford definite proof that benzyl benzoate is an intermediate in Cannizzaro's reaction. We can hardly assume that this ester is formed from benzyl alcohol and sodium benzoate in the presence of hydroxyl ion. With reference, however, to the two molecules of benzaldehyde from which it is produced

$$C_6H_5CHO + C_6H_5CHO = C_6H_6CO-O-CH_2C_6H_5$$
 (7)

benzyl benzoate represents the *completion* of an oxidation-reduction process. There must be antecedent steps.

It is well known that compounds containing the carbonyl group readily add sodium alkoxide.¹⁴ These addition products are known to show strongly additive properties towards other carbonyl compounds.¹⁵ We may write the following equation, using (OR) as equivalent to OH or to any alkoxide ion:

 $C_6H_5CH(OR)ONa + C_6H_5CHO = C_6H_5CH(OR)-O-CH(ONa)C_6H_5$ (8) This is entirely analogous to the formation of bromobenzyl benzoate, Equation 6.

The addition product assumed in Equation 8 is closely related to dibenzyl ether; it is a derivative of dihydroxy-dibenzyl ether.

$$C_6H_5CH(OH) - O - CH(OH)C_6H_5$$
 (9)

Dihydroxy-dibenzyl ether is a sort of glycol, and must be expected to undergo readily the typical hydroxyl shift. ¹⁶ Applying this metaklinic mechanism to the compound assumed in Equation 8, we have

This mechanism, while largely hypothetical and based on reasoning by analogy, seems to be the best available picture of Cannizzaro's reaction, at the present time. It accounts for the formation of mixed esters, as

¹⁴ The reaction is probably ionic, addition of OH⁻ or OR⁻. The hydroxide addition products are usually too soluble or too reactive to be isolated, but the work of Kohn and Tranton (Ref. 4) shows their existence in the present instance.

¹⁵ Compare Scheibler and Ziegner [Ber., 55B, 789 (1922)] for a recent and somewhat striking example of this type of reaction.

Lachman, This Journal, 44, 336 (1922).

observed by Claisen and by Tischtschenko. It also shows how a small amount of NaOR can act catalytically, as it does in the Claisen method of preparing benzyl benzoate. While the glycol shift, in general, is catalyzed by acids, aromatic glycols, such as benzopinacol, are also acted upon by alkalies. The separation of the hydroxyl groups is no barrier to the shifting process, for β -glycols, containing the group, -C(OH)-CH-C(OH-, also rearrange in typical fashion.

A similar mechanism will account for the behavior of dibenzyl and dibromobenzyl ether (Equations 2 and 5). As no hydroxyl groups are present, rearrangement is brought about by a shift of hydrogen, and a readjustment of electrons.

Conclusion

While it is advisable to postpone a discussion of the details of electron readjustment until further data have been collected, a few general rules may be stated, which seem to apply to the field covered in the present series of papers.

- 1. Hydroxyl groups attached to two neighboring carbon atoms (α or β -position) rearrange to give a carbonyl group, with loss of water.
- 2. A single hydroxyl group, at least in primary alcohols, tends to form a carbonyl group (aldehyde). The behavior of benzyl and of amyl alcohol illustrates two widely different modes of reaching the same end-point.
- 3. The carbonyl group tends to add hydroxyl or alkoxyl ion, and go over into carboxyl ion.
- 4. The readjustment of carbonyl to carboxyl necessarily involves the severance of a carbon-carbon bond; this may occur by *rupture*, producing two smaller molecules, or by rearrangement of the carbon chain. Other things being equal, the latter mode seems to be preferred.¹⁷
- 5. The preference for rearrangement over rupture applies also to reactions under Rule 1.

The phenomena of condensation, as in the case of the formation of aceto-acetic ester, seem to contradict Rule 3, but the contradiction is more apparent than real. Condensation is an intermediate step; and a continuation of the process, by the same reagents, leads to carboxyl formation.

One cannot but be struck by the almost purposeful behavior of some chemical substances. Who could have predicted the sequence shown in the conversion of benzyl alcohol into benzoic acid: benzyl alcohol, dibenzyl ether, benzaldehyde, Cannizzaro mechanism, benzyl benzoate, benzoic acid? Is there much difference between such a series of events, and what we call "instinct?"

¹⁷ Compare the behavior of dihydroxytartaric acid; This Journal, **43**, 2091 (1921). This conversion of carbonyl to carboxyl is also discussed, *ibid.*, **45**, 1533 (1923).

Summary

- 1. When aqueous alkalies act upon benzaldehyde, benzyl benzoate is a primary product.
- 2. Dihydroxy-dibenzyl ether is indicated as a prior intermediate, and a mechanism for its formation and its conversion into benzyl benzoate by a glycol-like rearrangement is given.
- 3. In the development of this problem, some properties of benzyl alcohol and of dibenzyl ether are studied.

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[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORIES OF CANADA]
THE ACTION OF CHLORAL ON CELLULOSE

By J. H. Ross and J. M. Payne Received May 7, 1923

Hefter¹ by heating a mixture of glucose and anhydrous chloral at 100° obtained two condensation products of chloral with glucose, namely chloralose (m. p., 187°) and parachloralose (m. p., 227°). Petit and Polonowski² and Hanriot and Richtet³ catalyzed the reaction by the addition of a small quantity of hydrochloric acid and obtained the same condensation products. Meunier,⁴ using a large quantity of concd. sulfuric acid, carried out the same condensation with chloral hydrate. In addition to the two chloraloses he isolated a dichloralglucose (m. p., 225°) and a chloralglucosan (m. p., 225°). F. H. Reichel⁵ treated glucosan and levoglucosan with chloral hydrate and sulfuric acid and obtained two additional dichloralglucoses (m. p., 268°, 85°). From glucosan he obtained parachloralose but no chloralose, whereas from levoglucosan he obtained chloralose but no parachloralose.

The object of the present investigation was to obtain chloral derivatives of cellulose which might be degraded to chloral-substituted glucoses and to compare them with similar derivatives from starch.

No definite products were obtained by the action of chloral or its hydrate on cellulose even in the presence of catalysts such as hydrochloric acid or zinc chloride. By the use of concd. sulfuric acid and chloral hydrate, as described by Meunier, cellulose yielded considerable quantities of chloral-glucoses but no chloral-substituted celluloses or cellulose dextrins.

Experimental Part

Fifty g. of surgical cotton was gradually stirred into a mixture of 100 g. of chloral hydrate and 100 cc. of concd. sulfuric acid contained in a beaker cooled in snow. The

- ¹ Hefter, Ber., 22, 1050 (1889).
 - ² Petit and Polonowski, Bull. soc. chim., [3] 11, 125 (1894).
 - ³ Hanriot and Richtet, ibid., [3] 9, 947 (1893); [3] 11, 37, 303 (1894).
 - ⁴ Meunier, Compt. rend., 122, 142 (1896); Ber., (Ref.) 29, 177 (1896).
- ⁸ Reichel, Thesis, University of Geneva, 1921. Pictet and Reichel, Helvetica Chim. Acta, 6, 621 (1923).

dissolution of the cotton was rapid with little discoloration and small evolution of heat. The reaction was then allowed to proceed at room temperature and occasionally stirred.

At the end of 2 hours a skin had formed at the surface of the liquid and on 12 hours' standing a thick, solid layer had formed there. This was removed and ground underwater in a mortar, giving a light gray flocculent, or at times granular, precipitate. The remaining liquid was poured into a large volume of cold water whereupon it gave a further quantity of the gray precipitate.

The precipitate was boiled in 600 cc. of water until it formed a soft gum, and only traces of chloral came off in the vapors. The water was decanted and a further 600 cc. containing from 5 to 10 cc. of coned. nitric acid was added and the mixture boiled for about 10 minutes, whereupon the water was decanted. The gum hardened as it cooled and was easily broken up under water in a mortar. Filtered and dried, it weighed about 69 g. When extracted with about 200 cc. of alcohol and filtered hot it left a residue which was further purified by solution in hot acetone from which it precipitated on cooling. This is named Fraction I.

From the alcohol as it cooled there precipitated a crystalline compound named Fraction II; when this is removed by filtration and the filtrate is concentrated to about $\frac{1}{3}$ of its original volume a further quantity of Fraction II is obtained.

The mother liquors were concentrated on a bath until two layers were formed. The upper layer was quite clear, the lower layer was dark brown. This latter solidified as it cooled. The upper layer was decanted and the solid dissolved in carbon tetrachloride from which a crystalline compound separated on cooling, named Fraction III. The carbon tetrachloride solution was evaporated to a thick sirup which hardened as it cooled and was named Fraction IV.

Fraction I.—This was obtained as triangular or 6-sided plates from hot acetone or alcohol; m. p., 268°. It is slightly soluble in hot acetone, pyridine, acetic acid, alcohol, or concd. nitric acid, and is insoluble in ether, chloroform, carbon tetrachloride, petroleum ether, water, or hot or cold alkalies. Its solution in pyridine is levorotatory. It does not reduce Fehling solution.

Analyses. Subs., 0.1465: AgCl, 0.2833. Subs., 0.1627: CO₂, 0.1621; H₂O, 0.0334. Calc. for $C_{10}H_{10}O_6Cl_6$ (Reichel's dichloral glucose): C, 27.40; H, 2.30; Cl, 48.59. Found: C, 27.17; H, 2.30; Cl, 47.84.

The mono-acetate was prepared from acetic anhydride and sulfuric acid. It crystallizes from ether in needles; m. p., 198° ; $[\alpha]_p - 12^{\circ}$ (c. $5.0)^6$ in CHCl₃.

Analysis. Subs., 0.1518: AgCl, 0.2178. Calc., mono-acetate: Cl, 44.25. Found: 44.30.

Upon methylation with dimethyl sulfate and sodium hydroxide, hairy needles were obtained from alcohol; m. p., about 200°; $[\alpha]_p - 17$ (c. 5.0) in 1:1 acetone-pyridine.

Analysis. Subs., 0.1612: AgCl, 0.3055. Calc. for $C_{11}H_{12}O_5Cl_6$: Cl, 46.98. Found: 46.89.

Fraction II.—Recrystallized from alcohol, this was obtained as needles; m. p., 225; $[\alpha]_b - 15$ (c. 1.2) in chloroform. It is not very soluble in carbon tetrachloride, and is insoluble in cold petroleum ether, water or alkalies. It does not reduce Fehling solution.

Analyses. Subs., 0.1377: AgCl, 0.2728. Subs., 0.1840: CO₂, 0.1830; H₂O, 0.0379. Found: C, 27.12; H, 2.30; Cl, 49.01.

Acetylation gives a product that forms thick, rectangular crystals from alcohol or ether; m. p., 126° ; [α]_D -21.4 (c. 4.67) in chloroform.

Analysis. Subs., 0.1567: AgCl, 0.2799. Calc. for C₁₂H₁₂O₇Cl₆: Cl, 44.25. Found: 44.19.

A concentration of 5 g. in 100 cc. of solution.

After methylation the substance became too soluble in organic solvents to purify by crystallization; m. p., about 110° ; $[\alpha]_{\rm p} - 23$ (c. 5) in chloroform.

Analysis. Subs., 0.1540: AgCl, 0.2820. Found: Cl, 45.46.

Fraction III.—This crystallizes from hot water in long needles that are soluble in most organic solvents; m. p., $135-136^{\circ}$; $[\alpha]_{\rm D}+32$ (c. 7.754) in benzene; $[\alpha]_{\rm D}+10.5$ (c. 7.617) in chloroform. The substance is soluble in cold, concd. nitric acid, but insoluble in alkalies.

It does not reduce Fehling solution even after it has been boiled with acids.

Analyses. Subs., 0.1433: AgCl, 0.2745. Subs., 0.1616: CO₂, 0.1471. H₂O, 0.0331. Found: C, 24.82; H, 2.29; Cl, 47.39.

Fraction IV.—This was a very impure fraction. The chief impurity seems to be Fraction II which may be precipitated from solution in alcohol by cautiously adding petroleum ether; m. p., about $74-75^{\circ}$; [α]_D +14 (c. 8.12) in chloroform. It is insoluble in water and alkalies.

Although the original substance does not reduce Fehling solution, reduction of this reagent takes place after the substance has been boiled with dil. acids. Nitric acid produces a compound that is precipitated by sodium hydroxide. Heated in a vacuum it loses 2.8% of its weight and then reduces Fehling solution. Its chlorine content is within 1% of that of a dichloralglucose.

Hydrocellulose, starch and glucose treated with sulfuric acid and chloral hydrate yield four fractions similar to those mentioned above. Glucose gives a lower yield of Fraction IV than do the other carbohydrates by this reaction. The liquors remaining from the precipitation of the dichloral sugars in water, when heated on the water-bath, precipitate a quantity of parachloralose. A large quantity of parachloralose is deposited from the water and dil. nitric acid after the precipitate obtained from starch and glucose has been boiled; this does not happen in the case of cellulose and hydrocellulose.

Conclusions

The action of chloral hydrate on starch and cellulose gives rise to identical dichloralglucoses.

Monochloralglucoses could not give rise to dichloralglucoses by condensation with a second molecule of chloral. The former have four free hydroxyls, which points to aldol condensation; while the latter possess but one free hydroxyl, which indicates acetal condensation throughout.

Since it has been claimed by previous workers in this field that parachloralose is produced by the α -anhydro-glucosidic linkage of d-glucosan and never by the β -anhydro-glucosidic linkage of l-glucosan, the formation of parachloralose from cellulose might indicate the pre-existence of one or more α linkages in the cellulose molecule.

Summary

1. Cotton cellulose was acted on by chloral hydrate using a large excess of sulfuric acid as a condensing agent. No chloral-substituted cellulose or cellulose dextrines were isolated, but from the reaction mixture four compounds were obtained, two of which corresponded in every way to two known dichloral glucoses (both levorotatory), m. p. 268° and 225°, respectively. The other two compounds gave analyses approximately

that of dichloral glucose (both dextrorotatory), m. p., 135° and 74°, respectively.

The same four compounds were formed in a similar manner from starch and glucose.

- 2. Acetylation and methylation of the two levorotatory compounds showed the presence of only one free hydroxyl group. No crystalline compounds were obtained by these reactions on the dextrorotatory compounds.
- 3. Parachloralose was formed when the crude water-insoluble products of starch and glucose, but not those of cellulose, were boiled. The soluble reaction products from all three, however, produced parachloralose when heated, after dilution, on the water-bath.

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MOLECULAR REARRANGEMENTS OF THE CAMPHOR SERIES. XIV. STRUCTURE OF ISOCAMPHOLACTONE¹

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Isocampholactone was first prepared by Noyes^{2a} by the action of nitrous acid on aminolauronic acid. It was later prepared by $\operatorname{Bredt}^{2b}$ in a pure condition by decomposing the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide. Noyes and Homberger³ oxidized isocampholactone with nitric acid and isolated two products, one the nitro-isocampholactone and the other a lactone acid which was the lactone of an hydroxy dicarboxylic acid and has the formula, $O = C - O - C_7 H_{11} COOH$. The amide of this lactone acid was prepared.

Nitro-isocampholactone was decomposed by dil. alkaline reagents forming an acid which has the formula $C_5H_8NO_2COOH$. Three carbon atoms and four hydrogen atoms were lost by the reaction but the other product of the reaction was not isolated. The amide of this acid was also prepared.

The structure of isocampholactone had not been determined when the investigation here described was begun. We have shown that it has Formula I.

¹ An abstract of a thesis presented by Philip K. Porter in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois, June, 1923.

^{2a} Noyes, Am. Chem. J., 17, 432 (1895).

^{2b} Bredt., Ber., 35, 1291 (1902).

³ Noyes and Homberger, This Journal, 32, 1665 (1910).

The lactone acid which was obtained by Noyes and Homberger³ was converted to the disilver salt from which the dimethyl ester was prepared. On treatment of the hydroxy ester with Beckmann's⁴ chromic acid mixture, which oxidizes primary and secondary hydroxy groups but not tertiary, the hydroxy group was shown to be tertiary and not secondary as it would be if no rearrangement had occurred. The lactone acid gives an amide which on treatment with sodium hypobromite is converted to a keto acid. The amide group and the hydroxy group are, therefore, on the same carbon atom. On treatment with sodium hypobromite, if the amino and hydroxy groups are on the same carbon atom, these split off ammonia, forming the keto group similar to the preparation of camphononic acid from camphanamide.⁵

This keto acid on treatment with methylmagnesium iodide regenerates isocampholactone and also forms another acid, which is probably the *trans*-hydroxy acid, as might be expected from the reaction. This compound was not fully identified however.

This series of reactions demonstrates that isocampholactone contains methyl groups in the 1,2,3 positions instead of the 1,2,2 positions of camphoric acid and should be called the lactone of 3-hydroxy-1,2,3-trimethyl cyclopentane-carboxylic acid.

The isomerism of campholactone and isocampholactone may be explained when we consider the second asymmetric carbon atom. Lauronolic acid, from which campholactone is formed, has a double bond which would cause the two methyl groups to be in the same plane, as shown in Formula II. On breaking the double bond to form the hydroxy acid, campholactone is formed and would have Structure III. Isocampholactone then would have the second methyl group in the *trans* position with reference to the other two methyl groups. We consider this explanation as very probable but not as definitely proved. The work here described proved the structure of isocampholactone conclusively but can not be considered conclusive concerning its stereometric configuration.

Nitro-isocampholactone, which evidently has the nitro group in the 2 position, was decomposed by sodium hydroxide in such a manner as to isolate the volatile reaction products; 60% of the calculated amount

⁴ Beckmann, Ann., 250, 325 (1889).

⁵ Lapworth and Lenton, J. Chem. Soc., 79, 1293 (1901).

of acetone was obtained. The only possible explanation of this reaction is shown in the following formulas:

The acid is either a cyclobutane derivative with a secondary nitro group or a cyclopropane derivative with a tertiary nitro group. The nitrous acid test⁶ applied to the amide, the acid or its ester gives a blue solution which is the test for a secondary nitro group. Secondary nitro groups would enolize and form a sodium salt when treated with sodium alcoholate. The amide and the methyl ester of the acid formed sodium salts quite easily in quantitative yields. Hydrolysis of the sodium salt of an enolic nitro group with dil. sulfuric acid would form a ketone if the nitro group is secondary, and a blue solution would be formed, while nitrous oxide would be given off. Hydrolysis of the sodium salt of the amide showed that no gas and no color was given to the solution. The original nitro acid was isolated from the reaction mixture.

Hydrolysis of the sodium salt of the methyl ester gave a deep blue solution and about $^{1}/_{3}$ of the calculated amount of nitrous oxide was obtained along with about the same amount of carbon dioxide. However, the original nitro acid was the only product isolated from the reaction. The keto acid which would form α -methyl-glutaric acid was not isolated, although the reaction seemed to have partially taken place. The nitrous acid test and the formation of the sodium salt of an enolic nitro group proves that this acid is a cyclobutane derivative and should be called 2-nitro-1-methyl-cyclobutane-carboxylic acid.

Experimental Part

Oxidation of Isocampholactone.—The isocampholactone required for these experiments was prepared by decomposing the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide; 65 g. of isocampholactone was heated for 72 hours

⁶ V. Meyer, Ann., 175, 93, 120 (1875).

⁷ V. Meyer, Ann., 256, 28 (1889).

⁸ Nef, Ann., 280, 273, 267 (1894).

⁹ Noyes and Taveau, Am. Chem. J., 32, 288 (1904).

with nitric acid, d. 1.27, 10 and 40 g. of nitro-isocampholactone was obtained; m. p., 121–122°; yield, 47.6%.

The mother liquors from the oxidation were evaporated to dryness. The viscous residue was dissolved in benzene upon evaporation of which crystals appeared; 11.7 g. of the lactone acid or the lactone of 3-hydroxy-1,2-dimethyl-cyclopentane-dicarboxylic acid was obtained; m. p., 136-138°.

Analyses. Subs., 0.1621: CO_2 , 0.3493; H_2O , 0.1010. Calc. for $C_9H_{12}O_4$: C, 58.67; H, 6.57. Found: C, 58.77; H, 6.98.

The Dimethyl Ester of 3-Hydroxy-1,2-dimethyl-1,3-cyclopentane-dicarboxylic Acid.—0.9666 g. of the lactone of 3-hydroxy-1,2-dimethyl-1,3-cyclopentane-dicarboxylic acid was dissolved in the calculated amount of sodium hydroxide by heating them together on the water-bath for 24 hours. The silver salt was obtained by adding an excess of silver nitrate; 1.9788 g. of salt was obtained or 90.5%.

Analysis. Subs., 0.2437: AgCl, 0.1683. Calc. for $C_9H_{12}O_5Ag_2$: Ag, 51.88. Found: 51.97.

The methyl ester was obtained by treating an ether solution of 1.1093 g. of silver salt with methyl iodide; 0.5343 g. of the ester was obtained; yield, 87.8%; b. p., 156–160° (25 mm.).

Analyses. Subs., 0.2053: CO₂, 0.4341; H₂O, 0.1439. Calc. for C₁₁H₁₈O₅: C, 57.39; H, 7.83. Found: C, 57.66; H, 7.86.

Beckmann's chromic acid mixture⁴ oxidizes primary and secondary hydroxyl groups but not tertiary hydroxy groups. On treating the ester with Beckmann's reagent, only a slight darkening in color (a test for a tertiary hydroxy group) was produced even after the mixture had stood for 12 hours.

The 3-Amide of the Lactone of 3-Hydroxy-1,2-dimethyl-1,3-cyclopentane-dicarboxylic Acid.—1.1559 g. of the lactone of 3-hydroxy-1,2-dimethyl-1,3-cyclopentane-dicarboxylic acid was heated for 5 minutes in a 50cc. flask with 1.3 g. of phosphorus pentachloride. The phosphorus oxychloride was distilled under diminished pressure and 5 cc. of dry ether was then added to dissolve the acid chloride. Cold concd. ammonium hydroxide (d., 0.9) was slowly added until the solution was strongly ammoniacal, after which the excess was evaporated under diminished pressure. The dry residue was dissolved in hot benzene, from which the amide crystallized. It was recrystallized from benzene; yield, 0.8638 g. or 75%; m. p., 162–163°.

3-Keto-1,2-dimethyl-cyclopentane-carboxylic Acid.—2.02 g. of the 3-amide of the lactone of 3-hydroxy-1,2-dimethyl-1,3-cyclopentane-dicarboxylic acid was dissolved in 14.3 cc. of a 10% solution of sodium hydroxide. After cooling the solution, the calculated amount of a cold sodium hypobromite solution was added. The reaction mixture was allowed to remain at room temperature for 12 hours and then heated on the waterbath for one hour. The cold solution was acidified with dil. sulfuric acid. Sodium sulfite was added to remove free bromine. The 3-keto-1,2-dimethyl-cyclopentane-carboxylic acid was extracted with ether and the extract dried over sodium sulfate. After distilling the ether, the acid was obtained as an oily residue from which 1.85 g. of the barium salt was obtained. The phenylhydrazone and the p-bromophenylhydrazone of the keto acid were prepared, both being oily materials. A crystalline hydrazone was not isolated.

Analyses. Subs. (Ba salt), 0.1194: loss at 120°, 7.20%. Calc. for $(C_8H_{11}O_3)_2$: Ba-2H₂O: 7.45.

¹⁰ Noyes and Homberger, This Journal, 31, 280 (1909).

¹¹ Ref. 3, p. 1666.

Subs., 0.1108: BaSO₄, 0.0572. Calc. for (C₈H₁₁O₃)₂ Ba: Ba, 30.69. Found: 30.37 Subs., 0.2159: BaSO₄, 0.1039. Calc. for (C₈H₁₁O₃)₂ Ba.2H₂O: Ba, 28.41. Found: 28.31.

Action of Grignard's Reagent on 3-Keto-1,2-dimethyl-cyclopentane-carboxylic Acid. Preparation of Isocampholactone.-Methylmagnesium iodide was slowly added to an ether solution of 3-keto-1,2-dimethyl-cyclopentane-carboxylic acid in the proportion of two moles of the former to one mole of the latter; 3.4 g. of methyl iodide was dissolved in 4 cc. of dry ether and the solution was added to 0.5837 g. of magnesium ribbon covered with ether. The methylmagnesium iodide thus formed was slowly added to an ether solution of 1.8665 g. of the keto acid. A complex was formed immediately. The reaction mixture was slowly refluxed for 20 minutes, after which it was cooled and the complex was decomposed by the addition of 2.5 cc. of 1:1 sulfuric acid. The ether extract was washed with a solution of sodium acid sulfite to remove the free iodine and then washed with a 10% solution of sodium carbonate to remove the unchanged keto acid and the trans-hydroxy acid which would be formed by the reaction, after which it was dried over sodium sulfate. On evaporation of the ether, a viscous residue was obtained which was further purified by steam distillation. The distillate was again extracted with ether and a solid was obtained which melted at 31-32°. A mixed melting point with pure isocampholactone was $31-32^{\circ}$; $[\alpha]_{D}^{26}-60.1^{\circ}$ (0.1406 g. in 5 cc. of absolute alcohol). Noves and Homberger¹² gave $[\alpha] - 63.1^{\circ}$.

To prove further its identity with isocampholactone, nitro-isocampholactone was prepared from this material by treatment with nitric acid, and was found to melt at 120–121°. A mixed melting point with pure nitro-isocampholactone was 120–121°; $[\alpha]_D^{26} - 88.6$ ° (0.0326 g. in 5 cc. of absolute alcohol). Noyes and Homberger¹² gave $[\alpha] - 85.4$. This reaction definitely proves the structure of isocampholactone; it should be called the lactone of 3-hydroxy-1,2,3-trimethyl-cyclopentane-carboxylic acid.

The sodium carbonate solution of the *trans*-hydroxy acid and unchanged keto acid was acidified and extracted with ether. An oily material was obtained. It was found that the calcium or barium salt of the hydroxy acid was difficultly soluble. This enabled a rough separation of the two acids to be made. A white solid was obtained which was acidic and melted at $96-97^{\circ}$; $[\alpha]_{10}^{28}$ — 37.5° (0.1681 g. in 5 cc. of absolute alcohol).

Treatment of this hydroxy acid with fuming hydrobromic acid failed to give the corresponding bromo acid. The presence of the hydroxy group was not positively shown, yet from its method of formation it seems quite probable that the material melting at 96–97° was a *trans*-hydroxy acid.

The Amide of 2-Nitro-1-methyl-cyclobutane-carboxylic Acid.—0.3257 g. of nitro-isocampholactone was slowly decomposed by 5 cc. of coned. ammonium hydroxide, 12 the excess being evaporated under diminished pressure. The dry residue was dissolved in hot benzene from which the amide crystallized; yield, 0.215 g., or 83%; m. p., 94-95°.

Analyses. Subs., 0.1686: CO₂, 0.2806; H₂O, 0.1013. Calc. for C₅H₈NO₂CONH₂: C, 45.5; H, 6.3. Found: C, 45.4; H, 6.73.

Subs., 0.0987; 15.8 cc. of N₂ (25°, 744.5 mm.). Calc. for $C_5H_8NO_2CONH_2$: N, 17.72. Found: 17.41.

2-Nitro-1-methyl-cyclobutane-carboxylic Acid.—Nitro-isocampholactone was decomposed by warming it with about 2N sodium hydroxide solution. When all of the nitro-isocampholactone had dissolved, the solution was acidified and the 2-nitro-1-methyl-cyclobutane-carboxylic acid was extracted with ether. It was converted to the barium salt and crystallized from water in long needles. The yields varied from 80 to 100%.

¹² Ref. 3, p. 1668.

In the first attempts to determine the other reaction product, the reaction was carried on in a flask sealed to a drying tube which was in turn connected to a combustion tube, and the volatile reaction product burned and analyzed. About 1/2 of the calculated amount of carbon and hydrogen which was lost by the reaction was accounted for by this arrangement.

Finally, 4.6931 g. of nitro-isocampholactone was decomposed by sodium hydroxide in a 100cc. flask which was connected to a 50cc. flask (cooled with ice and salt) by a tube that extended to the bottom of the flask. This flask was in turn connected to a 5cc. flask by a tube which extended to the bottom of the flask and was cooled by carbon dioxide snow and ether. The reaction mixture was slowly warmed on a water-bath until all of the nitro-isocampholactone had dissolved. Then it was slowly boiled until about 15 cc. of liquid had collected in the 50cc. flask. This material was boiled until about 3 cc. had collected in the 5cc. flask. The liquid material, which was acetone, was distilled; b. p., $56-58^{\circ}$; yield, 60%. It was identified as being acetone by the iodoform test and by the preparation of dibenzylidene acetone which melted at $111-112^{\circ}$.

The free acid was obtained from the barium salt by acidifying the solution of salt and extracting the acid with ether; m. p., $70-72^{\circ}$. The specific rotation was taken with a mercury-vapor lamp as the source of light at three different wave lengths, corresponding to the yellow line or $546.1\mu\mu$, the green line or $578\mu\mu$, and the blue line or $435\mu\mu$, and also with a sodium vapor light; $[\alpha]_{578}^{25}$, —101.51°; $[\alpha]_{435}^{25}$, —246.81°; $[\alpha]_{546.1}^{25}$, —119.3°; $[\alpha]_{546.1}^{25}$, —87.31°.

Analyses. Subs., 0.1381: CO_2 , 0.1485; H_2O , 0.0658. Calc. for $(C_5H_8NO_2COO)_2-Ba.2^1/_2H_2O$: C, 28.9; H, 4.2. Found: C, 29.3; H, 5.34.

Subs., 0.1657: BaSO₄, 0.0866. Calc. for (C₈H₈NO₂COO)₂Ba: Ba, 30.30. Found: 30.75.

Subs., 0.2168, 0.5331: BaSO₄, 0.1035, 0.2502. Calc. for $(C_5H_8NO_2COO)_2Ba.-2^1/_2H_2O$: Ba. 27.55. Found: 28.09, 27.62.

Subs., 0.1835: H_2O , 0.0178 (at 80° for 2 hours). Calc. for $(C_5H_9NO_2COO)_2Ba.-2^1/_2H_2O$: H_2O , 9.04. Found: 9.70.

Nitrous Acid Test for the Secondary Nitro Group.—According to V. Meyer, introus acid reacts with primary nitro groups to form a red solution of a nitrolic acid and with secondary nitro groups to form a blue solution of a pseudonitrole, while it does not react with tertiary nitro groups. The 2-nitro-1-methyl-cyclobutane-carboxylic acid and its corresponding amide and methyl ester were treated with nitrous acid and the blue color obtained in each case. The results of this test support the cyclobutane formula.

Silver Salt of 2-Nitro-1-methyl-cyclobutane-carboxylic Acid.—5.261 g. of the barium salt was dissolved in a small amount of water and an excess of silver nitrate was added; 4.122 g. of the silver salt was obtained; yield, 73.2%. The salt is slightly soluble in water and darkens on exposure to the light.

Analyses. Subs., 0.1104, 0.1281: AgCl, 0.0596, 0.0692. Calc. for C₆H₈NO₂-COOAg: Ag, 40.56. Found: 40.62, 40.65.

Methyl Ester of 2-Nitro-1-methyl-cyclobutane-carboxylic Acid.—4.122 g. of the silver salt was suspended in ether and a solution of 10 cc. of methyl iodide dissolved in 10 cc. of ether was added. The mixture was refluxed on a water-bath for 6 hours. The silver iodide was filtered off and the ether evaporated in a vacuum; 2.4335 g. of the ester was obtained; yield 90.7%. The ester boiled at $120-125^{\circ}$ at 5 mm. pressure with some decomposition. The specific rotation was taken with a mercury vapor lamp as a source of light at two different wave lengths, that corresponding to the yellow line or $578.1\mu\mu$ and that corresponding to the green line or $546.1\mu\mu$; $[\alpha]_{578.1}^{25}$, -90.2° ; $[\alpha]_{546.1}^{25}$, -93.2° ; $[\alpha]_{1.16907}^{25}$; n, 1.4416.

Treatment of the Amide of 2-Nitro-1-methyl-cyclobutane-carboxylic Acid with Sodium Alcoholate and the Hydrolysis of the Sodium Salt.—1.27 g. of the amide was dissolved in absolute alcohol and the calculated amount of sodium alcoholate was added. After this had stood at room temperature for two hours, two volumes of dry ether was added and the sodium salt was precipitated and filtered off. It was dried in a vacuum desiccator. The yield was quantitative.

Analyses. Subs., 0.1762, 0.1046, 0.1247, 0.1538: Na₂SO₄, 0.0630, 0.0393, 0.0446, 0.0564. Calc. for C₆H₉N₂O₃Na: Na, 12.77. Found: 11.58, 12.17, 11.66, 11.87.

Subs., 0.1071, 0.0897: NaCl, 0.0335, 0.0282. Calc. for $C_6H_9N_2O_3Na$: Na, 12.77. Found: 12.31, 12.35.

On hydrolysis of the sodium salt with dil. sulfuric acid, no gas was given off and the solution was only a faint blue. The solution was extracted with ether and a solid was obtained melting at $70-72^{\circ}$. A mixed melting point with pure 2-nitro-1-methyl-cyclobutane-carboxylic acid was $68-70^{\circ}$.

Treatment of the Amide with Two Molecular Equivalents of Sodium Hydroxide.—One g. of the amide was warmed with 5 cc. of a 10% solution of sodium hydroxide until the ammonia had ceased to come off. The residue was attached to a gas buret and acidified. A blue color was obtained which disappeared on warming. A gas was given off which caused a glowing splinter to burn, which is a qualitative test for nitrous oxide. About 1/3 of the theoretical amount of gas was given off. The reaction mixture was extracted with ether and an oily acidic material obtained. The silver salt was prepared.

Analysis. Subs., 0.0723: AgCl, 0.0386. Calc. for $C_6H_8NO_4Ag$: Ag, 40.56. Found: 40.18.

Recovery of the acid from the analysis gave a product melting at 71–72°. A mixed melting point with pure 2-nitro-1-methyl-cyclobutane-carboxylic acid was 69–70°.

Treatment of the Methyl Ester of 2-Nitro-1-methyl-cyclobutane-carboxylic Acid with Sodium Alcoholate and the Hydrolysis of the Sodium Salt.—2.27 g. of the ester was dissolved in absolute alcohol and the calculated amount of sodium alcoholate was added. After this had stood for a few hours, two volumes of dry ether was added, which precipitated the sodium salt. This was filtered off and dried in a vacuum desiccator. It is very unstable and decomposes easily. The yield, however, was almost quantitative. The analysis was made on very impure material because of decomposition.

Analyses. Subs., 0.1143, 0.0853, 0.1072: Na_2SO_4 , 0.0660, 0.0513, 0.0683. Calc. for $C_7H_{10}NO_4Na$: Na, 12.57. Found: 18.70, 19.48, 20.64.

Hydrolysis of the sodium salt with dil. sulfuric acid gave a blue solution, and about $^{1}/_{3}$ of the calculated amount of nitrous oxide was obtained that was identified by the test with a glowing splinter. About the same amount of carbon dioxide was also obtained. The reaction mixture was extracted with ether and the oily residue which was obtained was treated with barium carbonate, which separated the unchanged ester from the acids; these may be a mixture of the original nitro acid and the keto acid, which would break down into α -methyl-glutaric acid. The barium salts were fractionally crystallized. Since the barium salt of the nitro acid is difficultly soluble, the most soluble portion was converted into the silver salt.

Analysis. Subs., 0.1300: AgCl, 0.0921. Calc. for $C_6H_8O_4NAg$: Ag, 40.56; calc. for $C_6H_7O_3Ag$: 45.92; calc. for $C_6H_8O_4Ag_2$: 59.96. Found: 53.318.

The mixed acids obtained from a second experiment were warmed with acetyl chloride to form the anhydride of the α -methyl-glutaric acid and distilled. The low-boiling fraction, boiling at 130–140° (5 mm.), was taken. It was then boiled with water to regenerate the acid, and the silver salt was prepared.

Analysis. Subs., 0.0614: AgCl, 0.0428. Found: Ag, 52.46.

The analyses and the behavior of the reaction indicates that α -methyl-glutaric acid might have been formed, but in quantities too small to be isolated.

Summary

- 1. When isocampholactone is heated with nitric acid, the two main products formed are nitro-isocampholactone and a lactone acid. This lactone acid gives an amide which on treatment with sodium hypobromite is converted to a keto acid. This, on treatment with methylmagnesium iodide, regenerates isocampholactone and also probably forms a *trans*-hydroxy acid. This series of reactions demonstrates that isocampholactone contains methyl groups in the 1,2,3 positions and should be called the lactone of 3-hydroxy-1,2,3-trimethyl-cyclopentane-carboxylic acid.
- 2. A possible explanation of the isomerism of campholactone and iso-campholactone is given.
- 3. Nitro-isocampholactone on treatment with alkali gives almost quantitatively acetone and a nitro acid of 6 carbon atoms. The nitro group in this acid is secondary, as proved by the nitrous acid test and by the formation of a sodium salt of the enolic form of the nitro group in both the acid and its ester. This test proves that it is a cyclobutane derivative and should be called 2-nitro-1-methyl-cyclobutane-carboxylic acid.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SIMPLIFICATION OF THE GATTERMANN SYNTHESIS OF HYDROXY ALDEHYDES

By Roger Adams and I. Levine¹ Received May 21, 1923

The Gattermann synthesis of hydroxy aldehydes² which consists in saturating an anhydrous ether solution of certain phenols and anhydrous hydrogen cyanide with dry hydrogen chloride, sometimes with the addition of anhydrous zinc chloride, gives excellent yields of products which are readily purified. The method has proved to be invaluable for the preparation of certain intermediates in the synthesis of many natural compounds, and is still the only available process for preparing many representative hydroxy aldehydes. In spite of the ease with which the reaction generally takes place, its use in the laboratory is not as frequent as might be expected. This is due to the necessity of using anhydrous hydrogen cyanide, a product the preparation and handling of which in-

¹ This communication is an abstract of a thesis submitted by I. Levine in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

² Gattermann, Ber., 31, 1765 (1898); 32, 278, 284 (1899); Ann., 357, 313 (1907).
Morgan and Vining, J. Chem. Soc., 119, 177 (1921).

volve many disagreeable features. More recently,³ this method of preparation of the hydroxy aldehydes has been simplified somewhat by the generation of the hydrogen cyanide and its direct addition to the reaction mixture. Even this procedure does not make the preparation safe for any but the more experienced investigator. Such reactions as the Gattermann synthesis, involving anhydrous hydrogen cyanide, are consequently limited in their use.

Recently Karrer⁴ has shown that bromocyanogen may be substituted for hydrogen cyanide in the preparation of certain hydroxy aldehydes. The yields, however, do not appear to be as satisfactory as when hydrogen cyanide is used. Bromocyanogen is more conveniently made in the laboratory and more easily handled than anhydrous hydrogen cyanide, but even this product is extremely poisonous and much care must be used. Moreover, only a freshly prepared sample of bromocyanogen gives satisfactory results.

This research had as its object the modification of the Gattermann synthesis in such a way as to avoid using anhydrous hydrogen cyanide. Experiments in which hydrogen cyanide was replaced by certain of its salts have been carried out. Of these various salts, zinc cyanide would seem the most promising choice, since it would be changed during the reaction into a mixture of zinc chloride and hydrogen cyanide. Zinc chloride has already been shown by Gattermann to be an effective condensing agent for the reaction of the hydrogen cyanide with certain phenols in the presence of hydrogen chloride. The laboratory results have fully met the expectations. Very satisfactory yields have been obtained with resorcinol, α -naphthol, β -naphthol, or cinol and pyrogallol; in fact, the yields were similar to those obtained with anhydrous hydrogen cyanide. Undoubtedly any phenol that can be converted to an hydroxy aldehyde using the directions of Gattermann can be converted to an hydroxy aldehyde equally well by this slight but most convenient modification.

The preparation of zinc cyanide suitable for use in the reaction described above proved to be a problem in itself. Up to the present time zinc cyanide free from zinc oxycyanide has been made by the action of hydrogen cyanide upon zinc oxide or by other methods entirely unfitted for the present problem, the success of which depends upon the ease of preparation of the zinc cyanide. An easy method for preparing a satisfactory zinc cyanide for the Gattermann reaction was finally found. It consisted in treating an aqueous solution of sodium cyanide with magnesium chloride in order to precipitate the impurities of sodium hydroxide and sodium carbonate. Zinc cyanide was then precipitated by adding to the solution a molecularly equivalent amount of zinc chloride in alcohol. The product obtained is about 90% zinc cyanide and contains no impurity that interferes with the Gattermann synthesis.

 $^{^{3}}$ (a) Ziegler, Ber., 54B, 110 (1921). (b) Johnson and Lane, This Journal, 43, 354 (1921).

⁴ Karrer, Helvetica Chim. Acta, 2, 89 (1919).

The literature reports that zinc cyanide gradually decomposes on standing. The product made as described, if kept in a dry atmosphere, apparently decomposes only very slowly. After several weeks it was analyzed and showed a depreciation of about 2%. Nevertheless, it gave just as satisfactory results as when first prepared. No extensive experiments were made to determine just how long the zinc cyanide could be kept, since it can be so easily and quickly prepared.

Gattermann has also described the preparation of aldehydes from phenol ethers by the action of hydrogen chloride, hydrogen cyanide and anhydrous aluminum chloride on phenol ethers. Moreover, he has shown that certain hydroxy aldehydes which could not be made by the direct condensation of the phenol with hydrogen cyanide, hydrogen chloride and zinc chloride could be formed by the action of hydrogen chloride, hydrogen cyanide and anhydrous aluminum chloride upon the phenol. A modification of these last processes in such a way as to avoid the anhydrous hydrogen cyanide has proved successful and is now being studied in detail.

The authors are indebted to Dr. J. H. Reedy for suggestions in connection with the purification of the zinc cyanide.

Experimental Part

Zinc Cyanide.—To a 5% excess over 1 molecular equivalent of technical sodium cyanide calculated as 100% pure, regardless of its purity, dissolved in about 25% more than an equal weight of water, was added magnesium chloride solution until no more precipitate of magnesium hydroxide and carbonate formed (this requires an amount of magnesium chloride sufficient to precipitate a quantity of sodium carbonate equal in weight to about 7-8% of the sodium cyanide used). The precipitate was filtered off immediately and the filtrate added at once to 1 molecular equivalent of zinc chloride dissolved in as small an amount as possible of 50% alcohol. The zinc cyanide precipitated and was filtered off. When the magnesium hydroxide and carbonate were not removed immediately and the zinc cyanide precipitated at once, the reaction mixture turned dark until finally it became almost black. When the zinc chloride was added to such a colored solution the zinc cyanide formed was always colored. The zinc cyanide was washed on the filter with alcohol, then with ether and dried in a desiccator or in an airbath at 50° .

The only important precaution in this preparation is to insure an excess of zinc chloride over sodium cyanide. If the sodium cyanide is in excess, the zinc cyanide invariably precipitates as a sticky mass which is difficult to filter and unsatisfactory for the preparation of the hydroxy aldehydes.

The product was analyzed for the amount of cyanide present by titrating it with standardized silver nitrate solution, and was shown to be about 90% pure zinc cyanide. The remaining 10% was presumably for the most part sodium chloride, with small amounts of zinc chloride, magnesium chloride and perhaps traces of basic zinc cyanide. These do not interfere with the Gattermann reaction.

General Method of Preparation of the Hydroxy Aldehydes.—A 500cc. wide-mouth bottle was fitted with a stopper holding an efficient mechanical stirrer with a mercury seal, a reflux water condenser and an inlet tube, with wide mouth to prevent clogging from the precipitate, ex-

tending nearly to the bottom of the bottle. To this inlet tube was attached a safety bottle and to this a generator producing dry hydrogen chloride. To the top of the condenser was connected a tube leading into a wash bottle containing sulfuric acid; from this a tube was led to a safety bottle and from the latter a tube to the surface of a sodium hydroxide solution.

In the reaction bottle was placed 20 g, of the hydroxy compound in 150 to 200 cc. of dry ether. Sufficient dry zinc cyanide was then added, equivalent to 1.5 mol. for every mol. of phenol. The mechanical stirrer was started and dry hydrogen chloride was passed in rapidly. The zinc cyanide gradually disappeared with the formation of a milky solution (the milkiness being probably due to the sodium chloride present) and as more and more hydrogen chloride dissolved, the imide hydrochloride condensation product began to separate as a thick oil. In 10 to 30 minutes this oil turned to a solid. At the end of about 1.5 hours the ether was usually saturated with hydrogen chloride. When this point was reached, the stream of gas was passed in more slowly and stirring was continued for $^{1}/_{2}$ hour longer to be certain that all the phenol had reacted. The ether was decanted from the solid material and the imide hydrochloride then decomposed with water or dil. alcohol as described below.

The amount of ether used in the above reaction was somewhat greater than that suggested by Gattermann. It was found, however, that the colored by-products which invariably formed with these phenolic compounds were smaller in amount the larger the amount of solvent.

It was also possible to use dry chloroform in place of dry ether. Under these conditions the reaction went practically the same, but the crude products were somewhat more colored.

Resorcyl Aldehyde.—With resorcinol the reaction mixture turned pink and the solid material tended to be pink. Previous investigators advised the decomposition of the imide hydrochloride by boiling it with water for about 5 minutes and then allowing the product to cool. It was found that by this procedure the resorcyl aldehyde which separated amounted to about 70% of the calculated amount. It was found to be much more satisfactory to add about 100 cc. of water to the imide hydrochloride, raise the solution to the boiling point, filter the mixture and then immediately allow the filtrate to cool. In this way about a 50% yield of aldehyde was obtained. This was filtered and the filtrate was allowed to stand. In about 10 to 15 hours, more material separated which, upon filtration, amounted to about 45% of the calculated yield, giving a combined yield of 95%.

The resorcyl aldehyde obtained had only the slightest tinge of color and melted very sharply at 135–136° (Gattermann, 136°). By recrystallization from water with the addition of boneblack, a product absolutely free from traces of colored by-products was produced.

Orcinol Aldehyde.—The orcinol used in these experiments must be thoroughly dried to remove the water of crystallization which is ordinarily present. The reaction proceeded smoothly with the development of a pink color. No special precaution was necessary in the decomposition of the imide hydrochloride. It was merely boiled for

two to three minutes with 100 cc. of water, filtered and allowed to cool. The yield of product was about 85%; m. p., 178–180° (Gattermann, 180°). By a crystallization from water with the addition of boneblack a very pure product was obtained.

 β -Naphthol Aldehyde.—The imide hydrochloride was decomposed by boiling it with 100 cc. of water and an 85% yield of product was obtained, melting a few degrees below the correct point. After recrystallization from water with the addition of bone-black, a very pure product melting at 80–81° (Gattermann, 81°) was obtained.

 α -Naphthol Aldehyde.—In contrast to the hydroxy compounds described above where the reaction mixture was pink, that from α -naphthol became deep yellow. The imide hydrochloride was decomposed by boiling it with 700 cc. of 30% alcohol until complete solution took place; then the solution was filtered and allowed to cool. When water was used in this experiment, the α -naphthol aldehyde, because of its insolubility in water, tended to separate immediately and to prevent the smooth and complete decomposition of the imide hydrochloride. The product obtained as described formed in 72% yield and melted slightly low. More aldehyde could be recovered from the mother liquor. By recrystallization from water or 30% alcohol with added boneblack a very pure product resulted; m. p., 178° (Gattermann, 180°).

Pyrogallol Aldehyde.—The ether in the reaction mixture turned more deeply colored than when the other phenols were used, but the imide hydrochloride was light colored. It was decomposed by boiling it for two to three minutes with 400 cc. of water. The yield was about 45%, and the product melted at 158° (Gattermann, 158°). It can be obtained very pure by recrystallization from water containing boneblack.

Summary

- 1. Gattermann found that certain types of phenols condensed with hydrogen chloride, hydrogen cyanide and anhydrous zinc chloride to give compounds that hydrolyzed readily to form hydroxy aldehydes. A description of a method is given by which these same aldehydes can be formed in the same yields as found by Gattermann, but zinc cyanide is substituted for the anhydrous zinc chloride and hydrogen cyanide that he used.
- 2. Anhydrous zinc cyanide for this reaction was produced by treating aqueous sodium cyanide with magnesium chloride to precipitate the impurities of carbonate and hydroxide, filtering the precipitate and adding alcoholic zinc chloride to the filtrate.

URBANA, ILLINOIS

[Contribution from the Department of Physiology and Biochemistry, Medical College, Cornell University]

THE DETECTION OF PENTOSE, FORMALDEHYDE AND METHYL ALCOHOL

By James B. Sumner Received May 25, 1923

I have recently attempted to improve the well-known Bial's reagent¹ for pentoses so that it will keep, and have found that when the 6 g. of orcinol and 40 drops of 10% ferric chloride solution are dissolved together in 200 cc. of ethyl alcohol without the addition of hydrochloric acid, the solution is stable. Fifteen drops of this alcoholic solution, 5 cc. of the sugar solution and an equal volume of fuming hydrochloric acid are mixed and heated in boiling water. A clear blue color always develops when 1 mg. of arabinose or xylose is present. When more pentose is present a precipitate quickly forms. With less than 1 mg. the color is greenish. When considerable quantities of hexoses obscure the test the precipitate can be filtered off, washed with water and dissolved in alcohol, when some green color will be observed if the proportion of hexose to pentose is not too great. The absorption band is between the C and D lines.

While testing the specificity of this reagent I have found that it gives interesting results with formaldehyde. With 2 mg. of formaldehyde in 2 cc. of water, 10 drops of the orcinol solution and 2 cc. of concd. hydrochloric acid cause the immediate formation of a white precipitate, consisting of very small spheroids. With only 0.2 mg. of formaldehyde the precipitate does not appear for several minutes. Heating hastens its appearance. With still lower concentrations of formaldehyde no precipitate is formed and the solution becomes yellow upon heating. Acetaldehyde gives a similar precipitate with orcinol, but when a sufficient amount of water is present and the material is heated at once, no precipitate is formed unless a very large amount of acetaldehyde is present and the inside of the test-tube is covered with scratches.

When the material in the test with formaldehyde is heated for 15 minutes in boiling water, the precipitate turns brown and the addition of an excess of alkali causes it to dissolve to a pink solution, or if a large amount of precipitate was present, pink flocks will be formed. The precipitate formed by acetaldehyde does not turn brown upon heating and the addition of an excess of alkali causes it to dissolve to form a yellow solution.

With quantities of formaldehyde smaller than 0.1 mg., where there is no precipitate upon heating for 15 or 20 minutes, the addition of an excess of sodium hydroxide produces a pink or salmon color with an intense green fluorescence. So intense is this fluorescence that the test will readily

¹ Hawk, "Physiological Chemistry," Blakiston, 1923, 8th edition, 644.

show one part of formaldehyde in ten million parts of water. Acetaldehyde treated in the same manner gives a solution that shows no fluorescence at all.

Instead of heating with hydrochloric acid, the test can be heated directly with sodium hydroxide, but carried out in this manner is somewhat less delicate.

Another way of testing for the presence of formaldehyde is to add a few drops of an alcoholic solution of orcinol, omitting the ferric chloride, and 2 drops of 20% sodium hydroxide solution. The solution soon becomes pink when formaldehyde is present, owing to oxidation by atmospheric oxygen, the formaldehyde probably acting as an oxydase. As little as one part of formaldehyde in one million of water can be detected in this manner, but only if interfering substances are absent. Traces of copper also produce a pink color, and acetaldehyde causes the appearance of a greenishyellow color. Orcinol alone in the presence of alkali slowly develops a pink color.

While the production of the green fluorescence appeared to be too delicate to be put to use for the detection of methyl alcohol (after its oxidation to formaldehyde), the production of the white precipitate seemed suitable. I have found that this reaction can readily be used, and that its use is limited chiefly by the process employed to oxidize the alcohol. The application of a red hot copper spiral produces a very considerable amount of formaldehyde from pure ethyl alcohol. Using this procedure it is difficult to distinguish between pure ethyl alcohol and ethyl alcohol containing 1% of methyl alcohol.

Gettler² in his excellent review of 58 tests for the detection of methyl alcohol has recommended potassium dichromate and sulfuric acid as an oxidizing agent that forms very little formaldehyde from ethyl alcohol. I have tried this means of oxidizing the alcohols and have found it to be extremely satisfactory. As applied to the new method, removal of the chromium and sulfuric acid is not necessary, nor is it necessary to separate the acetaldehyde from the formaldehyde by fractional distillation. However, it is advisable to expel some of the acetaldehyde by heating in a large test-tube in boiling water, as acetaldehyde in large amounts sometimes forms a precipitate with orcinol. This seems to be due to the use of scratched test-tubes or test-tubes that have been attacked by hot phosphoric acid. The test-tubes must not be too narrow or the acetaldehyde will have difficulty in escaping. The amount of alcohol used in the test is 9 times greater than the quantity theoretically necessary to reduce all of the dichromate. An aqueous 0.5% solution of orcinol is used, and the addition of ferric chloride omitted.

The procedure is as follows.

² Gettler, J. Biol. Chem., 42, 311 (1920).

Place in a large test-tube which is 22 mm in diameter and free from scratches, 1 cc. of the suspected alcohol, 2 cc. of 6.7% potassium dichromate solution and 2 cc. of 1:2 (62%) sulfuric acid. Mix at once after adding the sulfuric acid and allow to stand at room temperature for about 10 minutes. The reduction of the chromic acid to blue chromic sulfate should take about 40 seconds, and if it takes much longer than this the alcohol used contains too much water. Add 15 cc. of distilled water, mix thoroughly and heat in boiling water for 10 minutes. Now add 5 mg. of orcinol in 1 cc. of water, mix very thoroughly and heat in boiling water for 30 minutes. If the alcohol contained 5% or more of methyl alcohol, a precipitate will be formed after about 5 minutes heating. With 1% of methyl alcohol a precipitate will form after 15 minutes' heating. The test will show methyl alcohol down to 0.5%, although in this case it may be necessary to heat for 30 minutes and then allow the solution to cool before a precipitate forms. If the precipitate is filtered off it will be seen to be distinctly brown or yellow.

Quantities of methyl alcohol smaller than 0.5% can be detected by precipitating the chromium by adding a slight excess of sodium hydroxide and heating. When this is filtered, the clear filtrate possesses a green fluorescence if even traces of methyl alcohol were originally present. This last procedure is of doubtful value, as it is to be expected that traces of methyl alcohol derived from pectinous substances may possibly be present in beverages from fruits.

The alcohol used in the test is obtained by distilling the suspected solution or beverage, using a Vigreux column to obtain as complete a separation from the water as possible. The temperature of the upper portion of the column should not be allowed to exceed 80°.

Formic acid, amyl alcohol, acetone and furfurol do not interfere with the test. Glycerol does not interfere because it is eliminated in the process of distillation; but if added to the alcoholic distillate glycerol gives a positive test if as much as 5 mg. is present. I believe, therefore, that the procedure for the detection of methyl alcohol can be used also for the detection of small amounts of glycerol. It is impossible at the present time to say that there are found in alcoholic beverages no substances capable of interfering with the detection of methyl alcohol as carried out by this method, but I have as yet found none and believe the method to be more time saving and more trustworthy than other chemical tests that have been proposed in such large numbers for the identification of methyl alcohol in alcoholic beverages.

Summary

- 1. A new method is proposed for using Bial's test for pentoses.
- 2. An extremely delicate test for formaldehyde is described.
- 3. A new method is given for the detection of methyl alcohol in alcoholic beverages.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

FLUORO-ACETYL DERIVATIVES OF SUGARS. II. OPTICAL ROTATION AND ATOMIC DIMENSION

By D. H. Brauns Received May 28, 1923

Introduction

Since the well-known discovery by Le Bel and van't Hoff of the coincidence of the presence of an asymmetric carbon atom in the molecule and the action of the latter on the plane of polarized light, organic and physical chemists have diligently studied this phenomenon. This marked interest has undoubtedly been inspired by the hope that this relation, coupled with ability to synthesize organic compounds of desired structure, would permit a further insight into the subject.

It is noteworthy that in proportion to the efforts made, the results are rather small. Van't Hoff's principle of optical superposition has given interesting results in the hands of Hudson^{2a} and Levene. ^{2b} The application of this principle and other related rules established by these authors are especially useful for determining the structure of organic compounds containing asymmetric carbon atoms. Nevertheless, the isolated and uncorrelated position of the property of optical rotation among other physical constants was not changed by these and numerous other investigations in which the influence of concentration of the solute, temperature, nature of the solvent and (most successfully) the wave length of the light (dispersion) were studied.3 It has been pointed out4 that the theory of Drude forms the basis for arranging and combining the facts regarding rotatory dispersion. A theory by Livens⁵ based on a general theory by H. A. Lorentz, establishing a relation between the optical rotation and the refractive index, is also regarded as promising for development. Inasmuch, however, as these theories have a purely physical basis without introducing a chemical viewpoint, it would appear that they are not capable of yielding a workable method for experimental treatment of the subject in its general form.6 This objection does not, however, hold for the

- ¹ For a discussion of the general rule for asymmetry and the limitations of the asymmetry of the molecule denoted by "asymmetric carbon atom," see Jaeger, *Bull. soc. chim.*, 33, 853 (1923).
- ² (a) Hudson, This Journal, 31, 66 (1909); 35, 1566 (1916); 39, 462 (1917); 40, 813 (1918). (b) Levene, Biochem. Z., 124, 42 (1921).
- ³ For literature see Stewart, "Stereochemistry," Longmans Green and Co., London, 2nd ed., 1919, p. 86.
 - 4 "Annual Reports on the Progress of Chemistry," London, 1914, p. 14,
 - ⁶ Ref. 3, p. 90.
- ⁶ See also Experim. Prüf. einiger Theorien des natürl. Drehungsvermögens opt. aktiver Lösungen, by Paul Wetterfors, Z. Physik, 8, 229 (1922).

theory of Guye (at least in its restricted form) which is an attempt to correlate the rotation and the difference in weight of the 4 asymmetric groups, without taking into account the distance of these groups from the center of gravity of the molecule. In its restricted form, the theory of Guye has been extensively tested by many organic chemists, the results disproving the validity of the theory.⁷

Theoretical Discussion

Notwithstanding these results, it seemed worth while to continue the search for some relation between the optical rotation and the weights of the asymmetric groups. Whereas former investigators changed an asymmetric group to a next higher one of the same homologous series and compared the rotations of the resulting derivatives, it appeared simpler to compare the rotations of derivatives which differ only in having an asymmetric halogen replaced by another halogen. With this type of derivatives the influence of the length of the chain may be eliminated. Furthermore, it is an important fact that the affinity of the halogens for hydrogen and oxygen changes regularly when they are compared successively according to their position in Mendeleieff's table; in addition to the direct union of the halogen with the carbon atom, secondary bonds to hydrogen and oxygen must also be taken into account. Since the influence of these affinities varies gradually and in a regular manner in the halogen series and only single atoms are considered, we may suppose that the position which the halogen occupies in the molecule is not changed when one halogen is replaced by another. Indeed, by comparing the optical rotations of chloro-, bromo- and iodo-tetra-acetylglucose, it was found that the increase in rotation is proportional to the increase in atomic weight. The data are compared in Table II, together with those for the analogous cellose derivatives. The fundamental thought of Guye, that the difference in weight of the asymmetric groups determines the rotation, so far as these data are concerned, is therefore supported by a comparison between the atomic weights and molecular rotations. It is evident, however, that a better agreement is obtained in the case of the specific rotations. It seemed worth while to extend this relation by preparing the analogous fluorine derivatives and including their values in the comparison. The preparation of the fluoro-acetyl derivatives of glucose, xylose and cellose and the determination of their specific rotations have been described by the author.8 Of the other fluoro-acetyl derivatives of sugars, which have been subsequently prepared, fluorotetra-acetylfructose will also be considered in this relation, inasmuch as the author has succeeded in preparing the corresponding bromotetra-acetylfructose in crystalline condition

 ⁷ H. Landolt, "Das optische Drehungsvermögen organischer Substanzen," Vieweg, Braunschweig, 2nd ed., 1898, p. 268. Also Tschugaeff, Ber., 31, 360, 1775, 2451 (1898).
 ⁸ Brauns, This Journal, 45, 833 (1923).

(see experimental part). Chlorotetra-acetylfructose has been previously9 prepared.

The results of comparison of the fluoro, chloro, bromo and iodo derivatives are presented in Table II, which shows that the data agree with the results of previous investigators in failing to support Guye's hypothesis. The increase in rotation from the fluorine to the chlorine derivative is much greater than the other differences, whereas the increase in atomic weight from fluorine to chlorine is much smaller than the others. The deviations found here immediately suggest a relationship with the atomic diameters. W. L. Bragg¹¹ derived these from the distances of the alternating atoms in the cubical crystals of the alkali halides. Bragg found that "the substitution of chlorine by bromine or bromine by iodine increases the distances between atomic centers by an amount which is approximately the same throughout the series of compounds, as the figures in italics show." Table I shows the results of Bragg's investigation.

Table I^{12} Interatomic Distances in Halides, in Ångstrom Units (10^{-8} cm.)

		United with-	
	Na	K	Rb
F	2.39	2.73	
	.42	.40	
Cl	2.81	3.13	3.28 °
	.16	.15	.16
Br	2.97	3.28	3.44
	. 26	.24	.22
I	3.23	3.52	3.66

For convenience we will take as an average for these increases 41, 16, and 24×10^{-10} cm. These values have been compared with the increase in optical rotation from the fluorine to the chlorine derivatives, etc., in Tables III and IV; the last column of Table III shows the differences

⁹ This Journal, 42, 1846 (1920).

¹⁰ In addition to fluorotetra-acetylfructose and the fluoro-acetyl sugar derivatives previously described (This Journal, 45, 833 (1923)) the author has prepared other fluoro-acetyl derivatives of other sugars; however, in the case of these latter derivatives, the other halogen derivatives necessary for comparison are not available. The preparation and properties of these latter fluorine derivatives will be reported later.

¹¹ Bragg, Science Progress, 16, 45 (1921).

¹² These figures are dimensions of ions, which have the outer shell of electrons complete, as in the case of the inert gases. No doubt these figures are equally applicable for the dimensions of the neutral atoms of the halogens. It is realized that these values are not final, nor do they agree exactly with those determined by other workers using different methods or holding different theories of atomic arrangement or structure. However, there seems to be no expectation, from the writings of many workers along this line, that it will be found that these values are not approximately correct. Even a critic of Bragg's views [Wyckoff, Proc. Nat. Acad. Sci., 9, 33–8 (1923)] gives values for the diameters of F, Cl, Br and I the differences between which are in the ratio of 41: 15:23, that is, not materially different from those adopted in this paper.

in atomic dimensions, reduced to approximately the same numerical values as those of the preceding columns.

Table II

Comparison of Specific and Molecular Rotations with Atomic Weight

			rivatives				erivatives			TD : 01
	Spec. r.	Diff.	Mol. r.a	Diff.	Spec. r.	Diff.	Mol. r.	Diff.	At. wt.	Diff.
C1	165.8		608		74.5		488		35.5	
		32.3		206		21.5		183		44.4
Br	198.1		814		96		671		79.9	
		34		244		29.5		265		47.0
I	232		1058		125.5		936		126.9	

^e The molecular rotations are divided by 100.

Table III

Comparison of Specific Rotations with Atomic Diameters

		Derivat	ives of			Respe spec.			A	t. dia diff		
	Glucose	Cellose	Xylose	Fructose		dif			r	educe		
F	+ 90.1	+ 30.0	+67.2	- 90.4			<u> </u>					
					76	45	98	71	76	45	98	71
CI	+165.8	+74.5	+165	-160.9^a								
					32	21	47	28	30	18	38	28
Br	+198.1	+ 96	+212	-189.1								
	•				34	30			44	26		
I	+232 •	+125.5										

^a The α -Cl derivative is taken, since we have to deal here with negative rotations [This Journal, 41, 1849 (1920)].

Table IV

Comparison of Molecular Rotations with Atomic Diameters

		——Deriva	tives of				ective . rot.		At. dia	m
	Glucose	Cellose	Xylose	Fructose			ffs.		diffs.	
F	+ 315	+191	+186	-315						
					293	297	300	274	41	
CI	+ 608	+488	+486	-589						
					206	183	233	188	16	
Br	+ 814	+671	+719	-777						
					249	265			24	
I	+1063	+936								

The following conclusions are derived from examination of these tables.

- 1. The differences in specific rotations vary in parallel manner with the differences in atomic diameters. Whereas the differences themselves are for the heavier cellose derivatives smaller and for the lighter xylose derivatives larger than for the glucose derivatives, they are nevertheless in all cases approximately proportional to the differences of the atomic diameters.
 - 2. Atomic dimensions may well play a role in physical constants

^b Starting with the (F-Cl) rotation-difference for each sugar the other values given are to one another as 41:16:24 (Table I).

pertaining to volume (specific gravity, solubility, refraction, etc.) as A. Sommerfeld ¹³ suggests. In the case of optical rotation, however, the relationship is less apparent. We may suppose that the distance between the halogen and the carbon atom is the determining factor; in this case it is strange, however, that the atomic weight is not more directly involved. It may be that the atomic dimension is an expression of the rotational momentum of the moving electrons in the atom. Unexpected is the result that the specific and not the molecular rotation is related to the atomic diameter in this simple way. After all, the nature of the action of a molecule on the light still remains to be determined. We have probably to interpret the results by supposing that the dimension of the halogen atom combined with the dimensions of the other asymmetric groups determines the asymmetric character of the molecule, and that the molecule by its entire weight (or with its total number of positive and negative electrons) brings its asymmetry to act upon the light.

Other relations in which atomic dimensions seem to play a role were observed by examination of the literature. In Tables V, VI and VII the author has inserted the values of the atomic diameter for purpose of comparison with the data quoted.

Chemical Affinity or Reaction Velocity

Holleman¹⁴ and co-workers determined quantitatively the amounts of 15 o- and p-nitrohalogenbenzene which are formed by nitrating monohalogenbenzene. The results are given in Table V.

Table V

Comparison of Atomic Diameter and the Formation of Nitrohalogenbenzenes

	Ortho %	Para %	Difference in % ortho derivs.	Ortho para	Successive diffs. in ortho para	Diff. at. di reduc	am.
F	12.6	87.4	17.5	0.14	29	17.5	29
Cl	30.1	69.9	7.5	.43	17	6.8	11
Br	37.6	62.4	3.5	.60	10	10.2	17
I	41.1	58.7	3.0	.70			

It is remarkable that the difference F-Cl is again much larger than Cl-Br. This suggests a relation to atomic dimensions. The difference Br-I does not agree with this assumption; the investigation of these iodine derivatives may, however, be subject to error owing to the possibility of secondary

¹³ Sommerfeld, "Atombau und Spektrallinien," 3rd ed., 1922, Vieweg (Braunschweig) p. 132.

¹⁴ Holleman, Rec. trav. chim., 32, 139 (1913).

¹⁵ The meta compound is produced only in traces.

reactions. Results of Lulofs¹⁶ who investigated a somewhat similar subject, measuring the velocity of substitution of halogen by an oxyalkyl group in halogen dinitrobenzenes, appear also to indicate that Holleman's results may be complicated by secondary reactions. Lulofs found the respective values 3.26, 1.89 and 0.455 for the chlorine, bromine and iodine derivatives; his data show for the difference Br-I a slightly greater value than for Cl-Br.

Boiling Points and Molecular Volumes of Corresponding Halogen Derivatives

Beekman¹⁷ determined the boiling points of the members of a series of corresponding halogen derivatives. Most of the molecular volumes were determined by interpolation from existing data and are, therefore, according to the author, only approximately correct. His results are compared with atomic dimensions in Table VI.

Table VI

Differences in Boiling Points and Molecular Volumes of Halogen Derivatives

Diff. in b. p. Diff. in mol. vol. Diff. in at, diam. Reduced

46.5	7.84	46.5	7.8
		20.0	
25.1	3.68	18.1	3.0
31.76	6.04	27 2	4.6
32.70	0,02		2.0
Meta 1	Derivatives		
		•	
30.6	8.2	30.6	8.2
20.9	4.25	13.0	3.2
23.5	8.1	17.9	4.8
Para I	Derivatives		
37	8.61	37	8.6
14	4.93	13	3.4
			· · · ·
• 14	6.89		5.0
	25.1 31.76 Meta I 30.6 20.9 23.5	25.1 3.68 31.76 6.04 Meta Derivatives 30.6 8.2 20.9 4.25 23.5 8.1 Para Derivatives 37 8.61 14 4.93	25.1 3.68 18.1 31.76 6.04 27.2 Meta Derivatives 30.6 8.2 30.6 20.9 4.25 13.0 23.5 8.1 17.9 Para Derivatives 37 8.61 37 14 4.93 13

The agreement with difference in atomic diameters is better for the boiling points than for the molecular volumes. Both values show, however, the exceptional place taken by the fluorine derivatives, as Beekman has already observed.

¹⁶ Lulofs, Rec. trav. chim., 20, 292 (1901).

¹⁷ Beekman, Rec. trav. chim., 23, 144 (1904).

Atomic Refraction

Swarts¹⁸ has determined the atomic refraction of several saturated and unsaturated compounds containing fluorine, chlorine and bromine. Table VII shows the results of this investigation, the numerical values of the atomic dimensions being reduced.

TABLE VII

Сомра	rison of Atom		ion Indici	es with A	TOMIC DIA	METERS
	Sat. compds.	Unsat. compds.	D	iffs.	Diff. at	
F	1.082	0.775				
			4.8	5.2	4.8	5.2
CI	5.9028	6.001				
			2.8	2.7	1.9	2.0
Br	8.762	8.759				

The agreement is not very striking, but shows that the difference in atomic refraction for Cl-F is nearly twice as great as for Br-Cl. 19

As has already been observed, the correlation of molecular volume and refraction with atomic dimension is not unexpected. Furthermore, the relative quantities of *ortho* and *para* derivatives which are formed in a reaction can be conceived to be dependent upon the atomic dimension (in this case, the influence of the distance of the halogen from the carbon atom). The relationship of specific rotation and atomic dimension suggests, however, the possibility that atomic dimension may also play an important role in a number of physical and chemical properties which are not supposed to be influenced by this factor.²⁰

18 Bull. acad. roy. med. Belg., [3] 34, 293 (1897).

Heydweiller [Ber. physik. Ges., 16, 722 (1914)] has compiled the atomic-refraction data for nearly all elements existing in solution in ionized condition. The values for the halogens (values for F and Cl are not very accurate) give the ratio (Cl-F):(Br-Cl): I-Br)=5.6:3.5:5.9, which shows that the (I-Br) value is decidedly too high for the atomic dimension relationship. It is possible that some complicating factor is involved.

While this paper was in the hands of the reviewing committee, another paper by Swarts has come to the writer's attention [J. chim. phys., 20, 30 (1923)] in which comparisons are made between atomic refraction and the same atomic-diameter values taken from Bragg which have been used in the present paper. Swarts found almost exact agreement in the case of the three heavier halogens, although fluorine showed considerable deviation.

²⁰ The investigation of optical rotation from this point of view will be continued for other types of halogen derivatives; such derivatives, representing four different sugar groups,—an aldohexose, a pentose, a disaccharide, and a ketose,—have already been tested. It is probable that further investigation will throw more light on the specific influence of the medium, concentration, etc., on the optical rotation; in the case of the sugar derivatives discussed in the present paper this influence is, however, relatively small as compared with the large differences in specific rotation. Other groups of related elements, such as (oxygen), sulfur, selenium and tellurium, may be examined in view of the fact that methods for obtaining corresponding sugar derivatives containing these elements (S and Se) are available. The derivatives already reported [Schneider and coworkers, Ber., 52, 2135 (1920), Wrede, Z. physiol. Chem., 115, 284 (1921), and many others of earlier date] do not permit a comparison.

Experimental Part

Fluorotetra-acetylfructose.—Starting with β -penta-acetylfructose²¹ the manner of preparation of this compound is the same as that described by the author for fluorotetraacetylglucose.³ The resulting colorless sirup crystallized readily when stirred with petroleun ether. Ten g. of β -penta-acetylfructose yielded about 7 g. of impure product. It was recrystallized by dissolving in 30 cc. of hot, 95% alcohol, filtering and washing the filter with about 15 cc. of hot alcohol. Crystals of moderate size were obtained; yield of pure substance, about 5 g.; m. p., 112°. A second and third recrystallization gave practically identical specific rotations. After the second recrystallization, 1.4803 g. made up to 25 cc. in chloroform produced a rotation in a 2dm. tube of 10.709 circular degrees to the left; hence, $[\alpha]_D^{20} = -90.43^\circ$. The compound is stable, colorless, odorless, and has a bitter taste; it is very slightly soluble in petroleum ether, slightly soluble in alcohol, and readily soluble in chloroform.

Analyses. Subs., 0.2151: CO₂, 0.3783; H₂O, 0.1046. Subs., 0.5819: CaF₂, 0.0620. Subs., 0.5378: 219.3 cc. of 0.1 N NaOH; 142.39 cc. of 0.1 N H₂SO₄. Subs., 1.8670, 3.6201, 5.1018: C₆H₆, 100; ΔF , 0.276°, 0.215°, 0.728°. Calc. for C₁₄H₁₉Q₉F: C, 47.98; H, 5.47; F, 5.43; 68.60 cc. of 0.1 N NaOH for AcOH; mol. wt., 350. Found: C, 47.97; H, 5.44; F, 5.19; 68.32 cc. of 0.1 N NaOH; mol. wt., 338, 347, 350.

Bromotetra-acetylfructose.—The preparation of this compound requires much care. At ordinary temperature it decomposes quickly, and special arrangements were required for analyzing and measuring the optical rotation of the pure substance. On account of the theoretical considerations involved, the attempt to prepare it which had been unsuccessfully made on previous occasions was resumed and finally led to the preparation of the pure crystalline substance and measurement of its rotation, as the excellent figures obtained on analysis show.

Six g. of powdered β-penta-acetylfructose was dissolved in 7 cc. of glacial acetic acid in a 25cc. volumetric flask with accurately ground stopper, by slightly warming the mixture on the steam-bath, the solution being then cooled in cracked ice to about 0°. A saturated solution of hydrogen bromide in glacial acetic acid was cooled in an ice-and-salt bath in a tube with ground stopper. This cold solution was used for quickly completing the volume of the fructose penta-acetate solution to about 25 cc., after which the stopper of the volumetric flask was replaced and the sirupy contents mixed by rotating the flask, the latter being kept in cracked ice for one hour. The solution was poured into about 30 cc. of chloroform²³ which had been cooled in an ice-and-salt bath in an Erlenmeyer flask with ground stopper. Without rinsing out the volumetric flask, the chloroform solution was poured in a mixture of ice water, cracked ice and a small amount of chloroform, contained in a separatory funnel.²⁴ The mixture was shaken and the chloroform solution drawn off into another separatory funnel and again shaken. This procedure was repeated twice, washing being omitted in order to permit more rapid work. The chloroform solution was dried over anhydrous sodium sulfate in an Erlenmeyer

²¹ This Journal, 37, 1283 (1915).

 $^{^{22}}$ For description of methods of analysis, see Ref. 8, p. 835. Saponification was performed by shaking with NaOH solution for $8^1/_2$ hours at 0° and titrating with $\rm H_2SO_4$ and phenolphthalein.

²³ The CHCl₃ had been specially purified by shaking it with some water, drying over Na₂SO₄, and distilling, the first and last fractions of the distillate being discarded.

²⁴ Two separatory funnels were made ready in this manner before the preparation of the compound was commenced. Arrangements for the Carius and acetyl determinations and for combustion were also made in advance, the only subsequent manipulation required being the introduction of the weighed substance.

flask (with ground stopper) in an ice-and-salt bath. After drying for about \$1/4\$ hour, the solution was filtered into a crystallizing dish and evaporated under a glass jar by means of a rapid current of air. The solution was cooled below \$0^{\circ}\$ by this rapid evaporation. A pure white crystalline preparation was obtained.\$25\$ A few cubic centimeters of absolute ether were stirred with the crystals and they were then pressed between hardened paper. The yield was more than \$4\$ g. of pure substance. Taking into account the manner of preparation, the reaction probably gives a quantitative yield. The \$4\$ accurate weighings necessary for combustion, Carius determination (including scaling of tube), acetyl determination, and preparation of the chloroform solution for measurement of optical rotation (performed in order stated), were made in about 25 minutes and gave the following results.

Analyses. Subs., 0.1614: CO₂, 0.2419; H₂O, 0.0685. Subs., 0.1885; AgBr, 0.0864. Subs., 0.5522: 219.3 cc. of 0.1 N NaOH; 152.4 cc. 0.1 N H₂SO₄; AgBr, 0.2518. Calc. for $C_{14}H_{19}O_{9}Br$: C, 40.87; H, 4.66; Br, 19.44; 152.6 cc. of 0.1 N H₂SO₄; AgBr, 0.2518. Found: C, 40.89; H, 4.75; Br, 19.50; 152.4 cc. of 0.1 N H₂SO₄; AgBr, 0.2518.

A solution of 0.4768 g. in chloroform made up to 25 cc. about 25 minutes after the preparation was obtained, produced a rotation in a 2dm. tube of 7.070 circular degrees to the left; hence, $[\alpha]_D^{20} = -186^{\circ}$. Another preparation of bromotetra-acetylfructose was examined immediately after the substance was prepared. A solution of 0.8188 g. of this preparation in 25 cc. of chloroform produced a rotation in a 2dm. tube of 12.397 circular degrees to the left; hence, $[\alpha]_D^{20} = -189.1^{\circ}$; this is taken as the specific rotation of the pure substance.

The substance was quickly recrystallized by making a saturated solution in pure ether in a weighing bottle, seeding with a few crystals, closing tightly with a rubber stopper and cooling in an ice-and-salt bath. The beautiful, large crystals which separated were quickly pressed between hardened filter paper. The specific rotation of this preparation was $[\alpha]_D^{20}$ —188.3°.

Bromotetra-acetylfructose is a very unstable substance. It can be obtained in pure crystalline form, but decomposition is already noticeable at room temperature after 25 minutes. In a few hours most of it is converted into β -tetra-acetylfructose. It may be kept in a pure ether solution, or better a pure chloroform solution, at -10° overnight, but decomposition is noticeable even under these conditions. The melting point is 65°. It is colorless, odorless, has a bitter taste, and is very soluble in the usual solvents and slightly soluble in petroleum ether.

Summary

In comparing the optical rotations of monohalogen acetyl derivatives of glucose, cellose, xylose and fructose, the differences F-Cl, Cl-Br, and Br-I are found to be approximately proportional to the differences in atomic diameter recorded by Bragg. It is remarkable that this simple relation holds for the specific but not for the molecular rotation. The

²⁵ While the chloroform solution was being evaporated to a thick colorless sirup (requiring about one hour), a small portion of the solution was evaporated on a watch glass, and by rubbing with a glass rod and finally adding ether or petroleum ether and subsequently evaporating, the resulting sirup was brought to crystallization. The crystals obtained were used for seeding the principal portion of the chloroform-free sirup.

method of preparation, properties, and analyses of fluorotetra-acetyl-fructose and bromotetra-acetyl-fructose are given.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OHIO STATE UNIVERSITY]

THE PREPARATION AND PROPERTIES OF 1-MERCAPTO-BENZOTHIAZOLE, ITS HOMOLOGS AND DERIVATIVES^{1,2}

By L. B. Sebrell and C. E. Boord

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The present paper comprises a study of the synthesis of 1-mercaptobenzothiazole and its derivatives which was made in connection with an investigation of the role played by these compounds when functioning as accelerators of vulcanization. Eight different mercapto-benzothiazoles were prepared and studied. Each of these substances excepting where the quantity of material was limited, were prepared by four separate methods. These methods were alike in that the reaction mixture was heated in an autoclave under pressure. The reaction mixtures were as follows: (1) the corresponding disubstituted thio-urea and sulfur; (2) the zinc salt of the corresponding aryl dithiocarbamic acid and sulfur; (3) the ammonium salt of the same acid and sulfur; (4) a mixture of the corresponding aryl amine, carbon disulfide and sulfur.

The first method has been described by Romani.³ The last three methods are new.

¹ This paper and one entitled: "A Study of 1-Mercapto-benzothiazole and its Derivatives as Accelerators of Vulcanization" being published in a current number of *J. Ind. Eng. Chem.* [15, 1009 (1923)] have been abstracted from the dissertation presented by L. B. Sebrell to the Graduate School of Ohio State University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, September, 1922.

² The system of nomenclature as outlined in \hat{C} . A. Decennial Index, 1-10, 2345, namely, omitting the sulfur and beginning the numbering with the carbon atom of the thiazole ring has been followed throughout this article.

³ The four methods of preparation described in the following pages as applied to 1-mercapto-benzothiazole and its three monomethyl derivatives, together with their disulfides and metallic salts were reported before the Organic Division of the American Chemical Society at the Birmingham meeting, April 6th, 1922. [(a) See Science, 56, 55 (1922).] Shortly afterward, an article by Romani, [(b) Gazz. chim. ital., 52, 29 (1922)] became available, describing the preparation of the three methyl derivatives by one of the methods, namely, heating the corresponding disubstituted thio-urea with sulfur. To him, undoubtedly, belongs priority of publication of a description of these three derivatives by this one method. He did not describe the disulfides.

Historical

1-Mercapto-benzothiazole was first obtained by A. W. Hofmann⁴ in an attempt to prepare the disulfilydryl derivative of thiocarbanilide by the action of carbon disulfide on o-aminophenol. He obtained the same substance by the action of sodium hydrosulfide on chlorophenyl mustard oil (1-chloro-benzothiazole) and also when carbon disulfide was caused to react with o-aminothiophenol disulfide. The product thus obtained, after recrystallization from alcohol, melted at 179° and was easily oxidized to a disulfide melting at 180°.

Jacobson and Frankenbacher⁵ while studying the formation of benzothiazoles, heated azobenzene with carbon disulfide in a sealed tube at 250° for 5 hours. The product melted at 174° but was identical with Hofmann's 1-mercapto-benzothiazole. The disulfide obtained by the oxidation of this product with potassium dichromate in acetic acid solution after recrystallization from benzene melted at 186°.

In order to verify the assumption that phenyl mustard oil is an intermediate product in the formation of 1-mercapto-benzothiazole from azobenzene, these authors heated the former substance in a sealed tube with sulfur for 5 hours. The yield of mercapto-benzothiazole thus obtained was equal to 45% of the weight of mustard oil used. The constitution of the thiazole was further established by fusion with potassium hydroxide, thus regenerating o-aminothiophenol.

Azobenzene when heated with phenyl mustard oil was found to yield 1-anilidobenzothiazole although the same substance could not be obtained by the direct action of aniline on mercapto-benzothiazole.

Rassow, Dohle and Reim 6 have shown that 1-mercapto-benzothiazole is formed by the action of sulfur on dimethylaniline.

Bedford and Sebrell⁷ as well as Bruni and Romani⁸ have independently described the preparation of 1-mercapto-benzothiazole by the reaction of thiocarbanilide with sulfur when heated under pressure. More recently Romani^{3b} has extended this method of preparation to the three monomethyl derivatives of 1-mercapto-benzothiazole. He recommends the use of an excess of sulfur and zinc oxide as a catalyst. Romani prepared the metallic salts of these methylated mercapto-benzothiazoles but not the disulfides.

Mechanism of the Reaction

Bruni and Romani,⁸ apparently following the lead of Jacobson and Frankenbacher, have sought to explain the formation of 1-mercaptobenzothiazole from thiocarbanilide, monophenyl-thio-urea and methylene-aniline upon the assumption that these substances first decompose to give phenyl mustard oil. They mention an alkali-insoluble residue, which apparently was not further investigated. It is shown in the experimental part of this paper that this insoluble residue consists chiefly of 1-anilidobenzothiazole and that it is formed in largest amounts when thiocarbanilide is used as the starting material. Indeed, it is almost entirely absent when ammonium phenyl-dithiocarbamate or the free aniline and carbon

- 4 Hofmann, Ber., 20, 1788 (1887).
- ⁵ Jacobson and Frankenbacher, Ber., 24, 1400 (1891).
- 6 Rassow, Dohle and Reim, J. prakt. Chem., 93, 183 (1916).
- ⁷ Bedford and Sebrell, J. Ind. Eng. Chem., 13, 1034 (1921).
- 8 Bruni and Romani, Giorn. chim. ind. applicata, 3, 351 (1921).

disulfide are used. The insoluble residue obtained when the zinc salt is used consists almost wholly of zinc sulfide.

If the formation of 1-mercapto-benzothiazole from thiocarbanilide is assumed to take place through its decomposition products, such as aniline and carbon disulfide or phenyl mustard oil, by virtue of their reaction with sulfur, then little or no 1-anilido-benzothiazole should be expected since these latter reactions form only small amounts of the alkali-insoluble residue. These facts seem to indicate that direct sulfurization of the thiocarbanilide offers the most satisfactory explanation for the simultaneous formation of 1-mercapto-benzothiazole and 1-anilido-benzothiazole. The formation of these two products may be readily understood by use of the following mechanism.

1. Thiocarbanilide may be assumed to be in equilibrium with its tautomeric form.

$$C_6H_5NH-C-NHC_6H_5$$
 $= C-NHC_6H_5$ $| SH$

2. This tautomeric form should occur as two geometric isomers, A and B.

3. When A is sulfurized and hydrogen sulfide eliminated 1-anilido-benzothiazole is formed.

4. When B is sulfurized and aniline eliminated 1-mercapto-benzothiazole is formed.

In the experimental part of this paper it is shown that the combined yield of these two products will account for between 90 and 96% of the thiocarbanilide used. These facts are of especial significance since Jacobson and Frankenbacher have shown that 1-anilido-benzothiazole is not formed by the action of aniline on 1-mercapto-benzothiazole.

The formation of 1-mercapto-benzothiazole from phenyl-dithiocarbamic acid and its salts is not so easily traced. It may be explained in one of three ways.

1. The dithiocarbamic acid derivative may decompose with the formation of phenyl mustard oil, which in turn reacts with the sulfur to form the mercapto-benzothiazole. This explanation would correspond to that offered by Jacobson and Frankenbacher⁵ and by Bruni and Romani⁸ to

account for the formation of the mercapto-thiazoles in other cases. The former workers obtained a 45% yield of 1-mercapto-benzothiazole by heating phenyl mustard oil with sulfur. In this Laboratory as high as 60% yields have been obtained by the same method. By reference to Table I it will be seen that phenyl-dithiocarbamic acid and its salts yield 75 to 80% of the same thiazole. It seems doubtful, therefore, whether phenyl mustard oil is an intermediate product in the formation of mercapto-benzothiazoles from phenyl-dithiocarbamic acid and its salts.

- 2. Phenyl-dithiocarbamic acid and its salts not only yield phenyl mustard oil but also undergo a second type of splitting with the formation of aniline and carbon disulfide. This is especially true of the ammonium salt, since thiocarbanilide is found among its decomposition products. Thiocarbanilide should be expected to react with sulfur yielding the mercapto-thiazole according to the scheme given above. Such a reaction would produce a large amount of an alkali-insoluble residue which experiment shows is not the case.
- 3. There is no a priori reason why phenyl-dithiocarbamic acid and its salts should not undergo direct sulfurization as readily as its anilide. The present authors believe this to be a more logical explanation and that the mercapto-benzothiazole is produced by the loss of the appropriate hydrosulfide from the addition product thus formed.

Experimental Part

Preparation of Materials.—The ammonium salts of the aryl dithiocarbamic acids were prepared by the method of Losanitch, by the reaction of the arylamine and carbon disulfide in the presence of ammonium hydroxide or ammonium sulfide in alcoholic solution. The rapid decomposition characteristic of these ammonium salts has caused many investigators to doubt their actual existence.

Ammonium phenyl-dithiocarbamate prepared in the presence of strong ammonium hydroxide is quite stable and after careful drying shows little tendency to decompose. By recrystallization from strong ammonium hydroxide it is obtained as long hexagonal crystals, which when carefully washed and dried have been kept for more than a year without evidence of decomposition. In the presence of moisture however it is slowly converted into thiocarbanilide, carbon disulfide and ammonia, as reported by Losanitch.

These ammonium salts may also be prepared by passing ammonia gas into a solution of aryl amine and carbon disulfide in benzene, but the method has no advantages over the one previously described.

The zinc salts of the aryl dithiocarbamic acids were prepared by adding a solution of zinc acetate in water or ammonium hydroxide to an aqueous solution of the corresponding ammonium salt. They may also be prepared by the method of Krulla¹⁰ who added the metallic oxide to a mixture of the aniline and carbon disulfide. The first method gives the purer product.

Thiocarbanilide and its substituted derivatives were prepared by the action of the aryl amine with carbon disulfide in the usual manner. These products were purified un-

⁹ Losanitch, Ber., 24, 3022 (1891); Ann., 166, 142 (1873).

¹⁰ Krulla, Ber., 46, 2669 (1913).

til the melting points varied not more than 3° or 4° from the highest recorded values in any case.

Apparatus.—The apparatus used in this work consisted of a steel autoclave mounted in an electric resistance oven. The autoclave, which had a capacity of 2 liters, was turned from tool steel and was capable of withstanding a pressure of 2000 pounds. The oven consisted of 3 heating elements specially wound from Chromel wire and mounted on a reinforced frame built up from Alundum cement. The heating unit was effectually insulated by packing in a mixture of asbestos and magnesite. Temperature control, secured by an external hot wire rheostat, was sufficiently exact to make it possible to reproduce any given set of temperature conditions. Temperatures up to 600° were easily obtained.

Procedure.—The substance used to prepare the thiazole was mixed intimately with one molar equivalent of sulfur and placed in the autoclave. Practically all runs were made by bringing the oven to a temperature of 390–400°, then lowering the autoclave to position and allowing the temperature of the reaction mixture to rise until the pressure reached a maximum. The pressure would rise gradually with the temperature to about 170–180° where the increase became much more rapid reaching a maximum at about 225–250°. The pressure generated varied with the substance used to produce the thiazole, being greatest with the ammonium salts and least with the disubstituted thio-ureas. Reproducing the heating conditions did not always give the same yield of product. Usually the autoclave was withdrawn from the oven immediately after the pressure reached the maximum to secure more rapid cooling, and when it was quite cold the accumulation of hydrogen sulfide was blown off and the autoclave opened.

Method of Purification.—The crude reaction product was removed from the autoclave by solution in warm dil. sodium hydroxide solution. This alkaline solution was submitted to steam distillation to remove any free aryl amine. The solution was then filtered from a residue of insoluble material and fractionally precipitated by the addition of small portions of hydrochloric acid. The first precipitates were very dark and carried down most of the coloring matter. The last fractions precipitated consisted of the 1-mercapto-benzothiazole in an almost pure form. The product was redissolved in sodium carbonate solution and reprecipitated further purification varied depending upon the nature of the product and will be described for each individual substance together with its physical and chemical characteristics.

Discussion of the Experimental Results

The data collected in the preparation of 1-mercapto-benzothiazole and 6 of its substituted derivatives are set forth in Table I. Not all of the runs made are listed, but those selected are typical. Failure to prepare all the thiazoles by each of the four methods was due to a lack of sufficient quantity of the aryl amines from which to prepare the necessary starting

materials. In such cases that method was selected which promised to yield the largest amount of easily purified product.

Table I

Data on the Preparation of 1-Mercapto-benzothiazoles

					3.5	3.5	37 077			
		Substances used	Used G.	Time Hrs.	Max. temp. °C.	Max. press. Lbs.	NaOH insol, G.	Yie G.	ld %	Product
	1	Thiocarbanilide	456	4.00	265	300	105.0	245.0	74.0	
	2	Ammonium phenyl-dithiocarba-			•					
		mate	263	1.50	224	1000	7.3	174.5	74.0	I-Mercapto-
	3	Zinc phenyl-dithiocarbamate	350	1.83	247	575	101.0	225.2	77.5	benzothiazole
	4	Aniline and carbon disulfide	93							100
			76	2.00	271	571	9.0	128.0	76.6	
	5 6	Di-o-tolyl-thio-urea	512	4.00	293	520	194.0	177.0	49.0	
	-	mate	170	1.42	253	1050	18.5	103.0	67.0	1-Mercapto-
	7	Zinc o-tolyl-dithiocarbamate	214	1.25	266	625	137.5	65.7	37.0	3-methyl-
	8	o-Toluidine and carbon disulfide.	105					00	0	benzothiazole
			76	1.58	255	675	34.7	80.4	45.5	
	9	Ammonium m-tolyl-dithiocarba-					5-111	0012	10,0	1-Mercapto-
		mate	186	1.00	242	625	15.5	116.6	69.5	4-methyl-
					1				30.3	benzothiazole
	10	Di-p-tolyl-thio urea	384	1.50	295	475	104.0	185.0	68.0)
	11	Ammonium p-tolyl-dithiocarba-							- 17 [24	1-Mercapto-
		mate	308	1.25	227	1050	22.8	199.2	71.5	5-methyl-
. :	12	p-Toluidine and carbon disulfide.	105			Mag. A				benzothiazole
			76	1.50	240	738	44.0	102.0	57.9	
	13	2,4,2',4' - Tetramethyl-diphenyl-								
		thio-urea	260	1.25	228	450	178.6	30.7	17.2	
	14	Ammonium o,p-xylyl-dithiocar-								1-Mercapto-
		bamate	198	1.70	220	1000	37.1	62.1	34.5	3,5-dimethyl-
	15	Zinc o,p-xylyl-dithiocarbamate	239	1.00	239	775	114.5	66.2	32.4	benzothiazole
	16	m-Xylidine and carbon disulfide	121							
			76	1.58	247	725	84.0	59.3	30.4	
- 6	17	Di-p-phenetyl-thio-urea	269	1.83	244	325	109.0	104.5	58.4	1-Mercapto-
	18	Ammonium p - phenetyl - dithio-								5-ethoxy-
		carbamate	339	1.10	206	1275 -	8.5	227.5	73.0	benzothiazole
	19	Zinc p-phenetyl-dithiocarbamate	288	1.58	246	550	125.0	147.7	59.3	(
. :	20	p-Phenetidine and carbon disul-	137						100	
		fide	76	1.30	249	455	49.0	117.4	55.6	
	21	p-Anisidine and carbon disulfide.	62							1-Mercapto-
			38	1.20	237	365	36.5	61.5	62.0	5-methoxy-
	1									benzothiazole

Runs 1 and 5 were made first, and without preheating the oven, thus accounting for the longer reaction time. In later runs the reaction time was shortened to avoid heat decomposition. The ammonium aryl-dithiocarbamates gave in general the best yields, but the products from the zinc salts contained less tarry material and were therefore more readily purified.

The more highly substituted the arylamine, the lower the yield of the thiazole so that only a 34.5% yield of the dimethyl derivative was obtained even from the ammonium salt of xylyl-dithiocarbamic acid.

The disubstituted thio-ureas always yielded large amounts of an alkaliinsoluble by-product. The yield of this substance is markedly lower when the ammonium salt of the aryl-dithiocarbamic acid or the aryl amine and carbon disulfide were used. In the case of the zinc salts the alkaliinsoluble product consisted almost wholly of zinc sulfide.

Nature of the Alkali-Insoluble Material

In the case of thiocarbanilide the alkali-insoluble part of the reaction product was found to consist largely of 1-anilido-benzothiazole. The purification of this anilido derivative proved to be so tedious that the separation of a similar derivative was not successfully completed in any of the other cases.

1-Anilidobenzothiazole.4—The alkali-insoluble residue from the thiocarbanilide-sulfur reaction mixture was dissolved in alcohol and the solution poured into dil. hydrochloric acid. A small amount of acid-insoluble substance was removed by filtration and the anilido derivative precipitated by the addition of sodium hydroxide. Fifty g. of the original residue gave 36 g. of the purified anilido derivative and 5 g. of the acid-insoluble substance, which proved to be mostly 1-mercapto-benzothiazole. After recrystallization from benzene the 1-anilido-benzothiazole was obtained as light yellow crystals melting at 154°. A mixture of this product with 1-anilido-benzothiazole prepared by the action of phenyl mustard oil on azobenzene gave the same melting point.

Analyses. Subs., 0.5470: 46.9 cc. 0.1 N H_2SO_4 . Subs., 0.5102: BaSO₄, 0.5293-Calc. for $C_{13}H_{16}N_2S$: N, 12.38; S, 14.16. Found: N, 12.00; S, 14.25.

Using the above data the calculated yield of pure 1-anilido-benzothiazole available from the 105 g. of alkali-insoluble residue from the thiocarbanilide in Table I is 75.6 g. or 16.5%. By combining this yield with the 73.3% of 1-mercapto-benzothiazole obtained, approximately 90.0% of the thiocarbanilide is accounted for. When one considers the losses incident to purification it is easy to conceive that the actual yield of the two derivatives is much higher, being about 96% on the basis of the crude products.

Disulfides

The disulfides of each of the mercapto-thiazoles described were prepared by the method of Hofmann.⁵ An alcoholic or alkaline solution of the mercapto-thiazole was oxidized by the gradual addition of an alcoholic solution of iodine. The resulting disulfide, insoluble in alcohol or alkalies, precipitated immediately, and after it was filtered, washed and dried was purified by recrystallization from the solvent indicated in each case.

Zinc and Lead Salts

The zinc salts of the mercapto-benzothiazoles may be prepared by either of two methods. A solution of the ammonium salt may be precipitated by the addition of a solution of ammonium zincate, or an alcoholic solution of the thiazole may be precipitated by adding an aqueous solution of any zinc salt. The first method gives the purer product.

Both the normal and the basic lead salts may be prepared, depending upon the method used. The normal lead salts were obtained by precipitating an alcoholic solution of the free thiazole or an aqueous solution of its sodium salt by an aqueous solution of any soluble lead salt. The basic lead salts were obtained by precipitating an alkaline solution of the mer-

capto-benzothiazole by a solution of lead hydroxide in an excess of sodium hydroxide. These salts were thoroughly washed, dried and subjected to analysis without further purification.

The zinc and lead salts of each of the several mercapto-benzothiazoles were prepared, but in only three cases were they actually analyzed and tested for their accelerating power as indicated in the following pages.

1-Mercapto-benzothiazole⁵ is soluble in alcohol, benzene and acetic acid. By recrystallization from dil. alcohol it was obtained as light yellow needles, melting at 177°.

Analyses. Subs., 0.7502: 44.8 cc. of 0.1 N $\rm H_2SO_4$. Subs., 0.1016: BaSO₄, 0.2840. Calc. for $\rm C_7H_5NS_2$: N, 8.38; S, 38.32. Found: N, 8.37; S, 38.38.

The Disulfide; an amorphous slightly yellow powder, melting at 176°; yield, 87%. The Zinc Salt; a white, amorphous powder.

Analysis. Cale. for $C_{14}H_8N_2S_4Zn$: N, 7.05; Zn, 16.45. Found: N, 7.21; Zn, 16.05. The Normal Lead Salt; a bright yellow powder.

Analysis. Calc. for C14H8N2S4Pb: Pb, 38.40. Found: 38.49.

THE BASIC LEAD SALT; an amorphous white powder.

Analysis. Calc. for C7H5NS2OPb: Pb, 53.05. Found: 52.35.

1-Mercapto-3-mtehyl-benzothiazole^{3b} after repeated recrystallizations from dil. alcohol and finally from 50% acetic acid was obtained as white needles melting at 186°.

Analyses. Subs., 0.7205: 41.2 cc. of 0.1 N H_2SO_4 . Subs., 0.1060, 0.1143: BaSO₄, 0.2720; 0.2929. Calc. for $C_8H_7NS_2$: N, 7.73; S, 35.36. Found: N, 8.00; S, 35.26, 35.21.

THE DISULFIDE; white needles from chloroform; m. p., 162°.

Analysis. Calc. for C₁₆H₁₂N₂S₄: S, 35.55. Found: 35.63, 35.48.

THE ZINC SALT; a white amorphous powder.

Analysis. Calc. for C16H12N2S4Zn: Zn, 15.37. Found: 15.35.

THE NORMAL LEAD SALT: an amorphous yellow powder.

Analysis. Calc. for C₁₆H₁₂N₂S₄Pb: Pb, 36.50. Found: 36.78.

THE BASIC LEAD SALT; an amorphous white powder.

Analysis. Calc. for C8H7NS2OPb: Pb, 51.24. Found: 51.50.

1-Mercapto-4-methyl-benzothiazole^{3b} was prepared only through the ammonium salt of *m*-tolyl-dithiocarbamic acid. After successive recrystallizations from 75% alcohol, 50% acetic acid and benzene, it was obtained as light yellow plates melting at 163°.

Analyses. Subs., 0.1585, 0.2270: BaSO₄, 0.4075, 0.5878. Calc. for C₈H₇NS₂: S, 35.36. Found: 35.30, 35.52.

THE DISULFIDE; white plates from benzene; m. p., 195°.

Analysis. Calc. for C16H12N2S4: S, 35.55. Found: 35.57; 35.65.

1-Mercapto-5-methyl-benzothiazole^{3b} was recrystallized twice from 50% acetic acid and finally from benzene. It forms fine, very light yellow crystals melting at 181°.

Analyses. Subs., 0.7234: 38.37 cc. of 0.1 N H_2SO_4 . Subs., 0.1860, 0.1985: BaSO₄, 0.4784, 0.5109. Calc. for $C_8H_7NS_2$: N, 7.73; S, 35.36. Found: N, 7.44; S, 35.39, 35.34.

THE DISULFIDE; This was insoluble in alcohol but soluble in benzene and chloroform, white needles from chloroform melting at 201–202°.

Analysis. Calc. for C16H12N2S4: S, 35.55. Found: 35.59.

THE ZINC SALT; a white amorphous powder.

Analysis. Calc. for C16H12N2S4Zn: Zn, 15.37. Found: 15.40.

1-Mercapto-3,5-dimethyl-benzothiazole was recrystallized several times from alcohol from which it separates in light yellow crystals melting at 250.5°. It is only very slightly soluble in acetic acid or benzene.

Analyses. Subs., 0.2050, 0.1888: BaSO₄, 0.4904, 0.4523. Calc. for $C_9H_9NS_2$: S. 32.82. Found: 32.85, 32.90.

THE DISULTIDE; fine white needles, m. p. 193°, obtained by repeated precipitation from chloroform with the gradual addition of alcohol.

Analyses. Calc. for C₁₈H₁₆N₂S₄: S, 32.99. Found: 33.02, 33.13.

1-Mercapto-5-ethoxy-benzothiazole was prepared by each of the four methods but only the ammonium p-phenetyl-dithiocarbamate yielded an easily purified product. Recrystallized from 75% alcohol and twice from benzene it was obtained as well-formed, long, cream-colored needles melting at 198° . It is only slightly soluble in benzene and other organic solvents.

Analyses. Subs., 0.1950, 0.1852: BaSO₄, 0.4303, 0.4044. Calc. for C₉H₉NOS₂: S, 30.33. Found: 30.31, 29.99.

Attempts to prepare the disulfide were unsuccessful.

1-Mercapto-5-methoxy-benzothiazole was prepared by each of the four methods but the product in all cases proved very difficult to purify. It was found that by rapidly heating the reaction mixture and rapidly cooling the autoclave a more easily purified product was obtained. Recrystallized from 70% alcohol and twice from benzene it forms light yellow needles melting at 2019.

Analysis. Subs., 0.1505: BaSO₄, 0.3546. Calc. for $C_8H_7NOS_2$: S, 32.48. Found: 32.37.

Attempts to prepare substituted mercapto-benzothiazoles from o-anisidine, the o- and p-chloro- and bromo-anilines and p-aminophenol were unsuccessful. Benzidine and carbon disulfide yielded an alkali-soluble product melting above 250°, which was not further investigated.

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Summary and Conclusions

- 1. The chemistry of the zinc and ammonium salts of phenyl-dithiocarbamic acid has been extended and the work of Losanitch verified.
- 2. Three new methods for the preparation of 1-mercapto-benzothiazole and its substituted derivatives have been described.
- 3. A fourth method previously described by one of us and independently announced about the same time by Bruni of Italy, has been extended to these derivatives.

- 4. The mechanism of the reaction involved in the formation of 1-mercapto-benzothiazoles by the action of sulfur on disubstituted thioureas is fully discussed. Experimental evidence is offered in support of the view that this reaction takes place by virtue of direct sulfurization of the *cis*-mercapto form of thiocarbanilide and subsequent loss of the aryl amine to form the mercapto-benzothiazole. It is also pointed out that sulfurization of the *trans*-mercapto form of thiocarbanilide and loss of hydrogen sulfide explains the simultaneous formation of anilido-benzothiazole.
- 5. Direct sulfurization and subsequent elimination of the corresponding hydrosulfide is offered as the best explanation of the formation of mercapto-benzothiazoles by the action of sulfur on the aryl dithiocarbamic acids and their salts.
- 6. Six substituted mercapto-benzothiazoles are described together with four of the corresponding disulfides.
- 7. Methods are given for the preparation of the zinc, normal lead and basic lead salts of the 1-mercapto-benzothiazoles and in three cases such salts are described.

Columbus, Onio

[Contribution from the Chemical Laboratory of the Johns Hopkins University] THE INFLUENCE OF SULFUR ON THE COLOR OF AZO DYES

By W. R. Waldron¹ and E. Emmet Reid Received June 11, 1923

The purpose of the present investigation was to study the effect of the sulfur atom and of the sulfone group, in various positions, on the color of azo dyes.

Brand² and coworkers found the —SCH₃ group to be strongly bathochromic as compared with —OCH₃ when introduced into azobenzene or into triphenyl carbinol, but they did not prepare any real dyes except to tetrazotize the dimethylether of o,o'-dimercapto-benzidine and couple it with salicylic acid, which gave a direct yellow on cotton, and with Hacid which gave a blue shade.

Several workers³ have mentioned that various amines containing sulfur give red dyes when diazotized and coupled with β -naphthol. The importance of thio-indigo and other dyes containing sulfur appeared to warrant a thorough investigation of the influence of sulfur in azo dyes.

Two classes of dyes have been considered. (1) Those derived from mono-amines, particularly those from p-thio-anisidine, CH₃SC₆H₄NH₂, and its sulfone, CH₃SO₂C₆H₄NH₂, which have been contrasted with the corresponding dyes from p-toluidine and p-anisidine, thus showing the

¹ From a dissertation by W. R. Waldron, 1922.

² Brand, (a) Ber., 42, 3463 (1909). Brand and Wirsing, (b) Ber., 45, 1757 (1912); (c) 46, 820 (1913). Brand and Stallmann, (d) Ber., 54, 1578 (1921).

² Nietzki and Bothof, (a) Ber., 27, 3262 (1894). Claasz, (b) Ber., 45, 1027 (1912).

relative effects of the groups CH3-, CH3O-, CH3S- and CH3SO2as auxochromes. The bases containing sulfur and the sulfone group have been prepared, diazotized and coupled with a number of standard intermediates, such as R-salt and chromotropic acid, and the resulting dves compared with the corresponding known dves containing methyl and methoxyl groups. In addition to the bases containing the CH₃S - group, a number have been made containing other radicals in place of methyl joined to sulfur, but the influence of the sulfur atom overshadows that of the radical. Methoxyl is a much stronger auxochrome than methyl; the CH₃S- group has been found to be stronger still, while oxidation of this group to the sulfone CH₃SO₂ - destroys this effect entirely, the group actually appearing as hypsochromic. (2) Those derived from diamines, which may be regarded as benzidine with various groups interposed between the two rings. A number of bases containing such groups as -S-, -SO₂-, -CH₂S-, -SCH₂S-, etc., between the two rings were made and dves prepared by diazotizing and coupling with standard intermediates. The bases most extensively compared were benzidine, thio-aniline, thio-aniline sulfone and one derived from mustard gas, NH2C6H4SCH2-CH2SCH2CH2SC6H4NH2. It was hoped that the dyes from these new bases would resemble those from benzidine, but it appears that the peculiar properties of benzidine dyes are lost when the two rings are separated. On the contrary, a base such as NH₂C₆H₄SCH₂CH₂SC₆H₄NH₂ resembles 2NH₂C₆H₄SCH₃. The -S- and -SO₂- groups have the same effects in the diamino as in the mono.

In all the dyes made, the sulfur atom has a decided bathochromic effect, provided it is joined directly to the ring carrying the azo chromophore group, but it has little effect when it is separated from the ring by even a methylene group. In the dyes derived from the two isomeric bases, $\mathrm{NH_2C_6H_4SCH_2C_6H_5}$ and $\mathrm{NH_2C_6H_4CH_2SC_6H_5}$, the sulfur has a decided effect in the first case and practically none in the second.

As intermediates, a large number of new compounds have been prepared, along with some that have been previously described. The general method has been to obtain the nitro compound by condensing a halide with the sodium salt of p-nitro-thiophenol, or p-nitrobenzyl bromide with the sodium compound of a mercaptan. One portion of the product has been reduced to the amino-sulfide and the other portion oxidized to the sulfone and then reduced to the amino-sulfone. The details of the numerous preparations are given in tables. The diazotizing, coupling and dyeing were according to accepted methods.

Materials

The p-nitrobenzyl bromide used in this work was prepared following the method of Brewster⁴ with slight modifications. p-Nitro-toluene was brominated in the sunlight

⁴ Brewster, This Journal, 40, 406 (1918).

in Pyrex glass at the boiling point of carbon tetrachloride which was used as solvent, a trace of iodine being used as a bromine carrier. When the amount of solvent recommended by Brewster is reduced to half, the most of the p-nitrobenzyl bromide crystallizes on cooling to 5° , leaving the oily by-products in solution. By one recrystallization from three parts of alcohol the compound was obtained in long needles, m. p., 99° . By removing the carbon tetrachloride first, the product was contaminated with oils which necessitated two or three recrystallizations before it was obtained pure; yield, 55-65%.

p-Nitro-thiophenol was first prepared by Willgerodt.⁵ The preparation has been studied and improved by Mayer,⁶ Kehrmann and Bauer,⁷ Brand⁸ and Blanksma.⁹

In the following work the sodium salt of the mercaptan was prepared following in part the methods of Wohlfahrt, ¹⁰ Mayer, ¹¹ and Brand. ¹² Brand states that this salt is not stable above 100° and that its solution oxidizes rapidly in the air. We isolated the salt readily in a very pure state, dried it at 60°, and found that it keeps indefinitely without apparent change.

One gram-mole of p-nitrochlorobenzene is suspended in 150 cc. of alcohol, to which is added slowly with mechanical stirring 1 mole of sodium disulfide (100% excess) in 600 cc. of water. The reaction is exothermic and the mixture boils by the time all of the disulfide has been added. After the charge has been stirred for 5 minutes it is poured into 2 liters of cold water. By this time practically all of the p-nitrochlorobenzene has reacted; the solution contains a mixture of the sodium salt of the mercaptan and the disulfide. After dilution, the disulfide is filtered off and the red solution acidified, precipitating the impure free mercaptan. This is filtered off at once and dissolved in 500 cc. of boiling 5% sodium hydroxide solution. The hot alkaline solution is filtered to remove any disulfide or impurities carried by the mercaptan. It is allowed to cool and saturated sodium hydroxide solution is added causing an almost complete precipitation of the sodium salt in large red plates. The disulfide residue obtained is reduced with sodium hydroxide and sodium sulfide, following the procedure of Brand, and the solution containing the sodium salt is treated in the same way as described above. The yields obtained average 60%, being equally divided between the two steps in the process.

The p-nitrotoluene, p-nitrochlorobenzene and a large number of naphthalene intermediates used in this work were obtained through the courtesy of E. I. du Pont de Nemours and Company. We are also indebted to them for much information as to carrying out various processes.

I. (a) Alkyl and Aryl para-Nitro-thiophenyl Ethers, RSC₆H₄NO₂

The methyl, ¹⁸ ethyl ¹⁴ and benzyl ¹⁵ compounds had previously been made, the first two by the same method as used here.

The alkyl derivatives (including benzyl) were made by dissolving 0.1 mole of the halide in 75 cc. of 95% alcohol and adding 0.105 mole of sodium

- ⁵ Willgerodt, Ber., 18, 331 (1885).
- ⁶ Mayer, Ber., 42, 3050 (1909).
- ⁷ Kehrmann and Bauer, Ber., 29, 2362 (1896).
- ⁸ Brand, Ber., 42, 3463 (1909); 45, 1757 (1912); Ger. pat. 228,868.
- Blanksma, Rec. trav. chim., 20, 138 (1901).
- 10 Wohlfahrt, J. prakt. Chem., [2] 66, 551 (1902).
- 11 Mayer, Ber., 42, 3050 (1909).
- 12 Ref. 2c. p. 822.
- 18 Blanksma, Rec. trav. chim., 20, 400 (1901). Ref. 11.
- 14 Blanksma, Ref. 13, p. 403.
- ¹⁵ (a) Fromm and Wittmann, Ber., 41, 2267 (1908). (b) Kulenkampff, Inaug. Dissertation, Freiberg, 1906.

p-nitro-thiophenate made into a thick paste with water. The mixture is stirred vigorously for 5 minutes and then heated to boiling on a waterbath. The reaction is soon complete, the solution remaining reddish on account of the slight excess of sodium mercaptide. The less soluble solid products separate as the solution is cooled to 0° . The oils were obtained by distilling most of the alcohol, washing the residue with water and dil. alkali and finally drying with calcium chloride. The solids are best recrystallized from 50--80% acetic acid.

The details of the preparations together with the properties of the products are given in Table I. Methyl iodide, benzyl and phenacyl chlorides were used and the bromides of all of the other alkyls.

TABLE I

			para-Nitro-thiophenol	

	NO ₂ C ₆ H ₄ SNa G.	Halide	-Yiel	d-	M. p.	d ₂₅	-	
Alkyl	G.	G.	G.	%	°C,	-25	Properties	
Methyl ^a	17.7	14.2	12	71	72		Yellow needles	
Ethyl ^a	8.9	7.8	7	76	44		Yellow needles	
isoPropyl	17.8	12.3	15.5	76	44.5		Yellow needles	
Propyl	17.8	12.3	14.	71		1.1963	Brown oil	
isoButyl	35.5	27.4	33	78		1.1573	Brown oil	
Butyl	17.8	13.7	15	71	• • .	1.1625	Brown oil	
isoAmyl	17.8	15.1	15	70		1.1335	Brown oil	
Benzyla	178	12.6	18	73	123		Yellow plates	
Phenacyl	6	5.2	9	98	118		Yellow plates	
Hydroxyethyl.	35.5	16.2	33	82	59		Yellow needles	

 $^{^{\}rm o}$ Previously prepared, the melting points given in the literature are: methyl 67° and 71–72°, ethyl 40° and benzyl 123°.

Four of the thio-ethers are oils having slight but peculiar odors. They could not be distilled even at 5 mm. pressure on account of decomposition. All of the compounds are insoluble in water.

Sulfur analyses were made according to the method of Parr. 16

isoPropyl	NO ₂ C ₆ H ₄ SCH(CH ₃) ₂	Calc. 16.27	Found 16.25
Phenacyl	NO2C6H4SCH2COC6H5	11.76	11.88
Hydroxyethyl	NO2C6H4SCH2CH2OH	16.08	16.28
Bromo-ethyl	NO ₂ C ₆ H ₄ SCH ₂ CH ₂ Br	12.23	12.94

Fromm and Wittmann¹⁷ obtained p-nitrophenyl-thioglycolic acid by condensing the mercaptide with sodium chloro-acetate. This and the corresponding amine have also been prepared by Friedlaender and Chwala.¹⁸ They made the acid from p-nitro-chlorobenzene and thioglycolic acid with sodium hydroxide. We obtained it from p-nitro-thiophenol and chloroacetic acid in the presence of alkali.

The same reaction took place with glycol-chlorohydrin and sodium

¹⁶ Parr, J. Ind. Eng. Chem., 11, 230 (1919).

¹⁷ Ref. 15a, p. 2273.

¹⁸ Friedlaender and Chwala, Monatsh., 28, 274 (1907).

p-nitro-thiophenolate, forming the thio-ether of monothioglycol as yellow plates; m. p., 59°. On refluxing this compound with hydrobromic acid for several hours the bromide NO₂C₆H₄SCH₂CH₂Br was obtained in 86% yield as yellow plates; m. p., 58°.

The phenyl derivative was readily prepared in 95% yield from p-nitro-chlorobenzene and the sodium salt of thiophenol in alcoholic solution. It had previously been made by Kehrmann and Bauer¹⁹ by eliminating the amino group from p-nitro-p'-amino-diphenyl sulfide.

Esters of p-Nitro-thiophenol

Esters were readily obtained by using benzoyl chloride, phosgene and thiophosgene. These were recrystallized from about 50% acetic acid as they are too soluble in strong acetic acid. Sulfones could not be obtained by oxidizing these esters. On reduction, only the *p*-nitrophenylthiol-benzoate (6 g.) gave the desired amine (4 g.; 75%); m. p., 115°. The calculated percentage of sulfur was 14.01; that found, 14.10.

PREPARATION AND PROPERTIES OF ESTERS OF para-Nitro-thiophenol

						Sul	ur	
Formula	NO ₂ C	G. G.	G.	ield— %	М. р. °С.	Calc.	Found %	Properties
NO2C6H4SCOC6H5		17.7	14	54	123.7	12.39	12.42	Yellow plates
$(NO_2C_6H_4S)CO$		18	11	64	174.5	19.04	19.46	Yellow powder
$(NO_2C_6H_4S)CS$		18	10	55	141	27.28	27.10	Buff powder

The chlorides of p-toluene-sulfonic and m-nitrobenzene sulfonic acids were used in the same way but the desired esters could not be obtained.

(b) Alkyl and Aryl para-Amino-thiophenyl Ethers, RSC₆H₄NH₂

The methyl²⁰ compound had been prepared by the reaction of p-aceto-amino-thiophenol on methyl sulfate with the subsequent removal of the acetyl group, and the ethyl,²¹ phenyl²² and benzyl¹⁵ compounds by the reduction of the corresponding nitro compounds with tin and hydrochloric or acetic acid. We considered that reductions with iron and a trace of acetic acid, though much slower, would obviate the danger of splitting the molecule at the sulfur atom. The method with iron was found to be quite satisfactory.

To 5 g. of the nitro compound is added 15 g. of iron dust, 0.1 cc. of concd. acetic acid and 100 cc. of water, and the charge is stirred for 10 hours at $85-90^\circ$. At the end of this time the mixture is made alkaline with sodium carbonate and filtered. The filtrate is shaken with benzene to obtain the oil and the iron residue extracted four times with hot benzene. The combined extract is distilled on a water-bath, the last traces of benzene being removed by applying a vacuum. The oil is then added to 100 cc. of 5% sulfuric acid and the difficultly soluble sulfate so obtained is recrystallized from boiling

¹⁹ Kehrmann and Bauer, Ber., 29, 2364 (1896).

²⁰ Zincke and Jörg, Ber., 42, 3368 (1909); b. p., 140° (15 mm.).

²¹ Monier-Williams, Soc., 89, 278 (1906); b. p., 280-281°.

²² Ref. 19; m. p., 93°; acetyl, 146°.

water, a small amount of diatomaceous earth being added to remove any tar. The yields in all cases are 85-90%.

All of these bases except the phenyl are oils with practically no odors; they darken rapidly in the light and the solubility of the sulfates decreases rapidly with increase in molecular weight, the sulfate of the benzyl compound being almost insoluble in boiling water. The hydrochlorides are much more soluble and may be obtained by saturating the benzene solution of the base with dry hydrogen chloride.

Details of the preparations and the properties of the compounds are given in Table II. The sulfates of the bases were analyzed by dissolving in hot water and adding barium chloride solution, the figures given being the sulfur in the sulfate ion.

			- 2 - 0					
	Nitro						Sulfur	
Alkyl or aryl	compound G.	G. Yie	eld− %	М. р. С.	d_{25}^{25}	Cale.	Found %	
Methyl ^a	10	8	97		1.1425			
Ethyl ^a	5	4	95		1.1010			
isoPropyl	10	7	82			7.41	7.45	
Propyl	10	7.5	88			7.41	7.30	
isoButyl	10	8	93		1.0421	6.96	7.08	
Butyl	10	8	93			6.96	7.08	
isoAmyl	. 10	8	92			6.57	6.62	
Phenyl ^a	18.5	10	62	95.8				
Benzyl ^a	12	8.5	81		1.1321			
Phenacyl	. 9	7	87	111.5		13.19	13.59	

^a Prepared by other authors; the phenyl is given as melting at 93° and 95°.

(c) Alkyl and Aryl para-Nitrophenyl Sulfones, RSO₂C₆H₄NO₂

Three sulfones of this series have been prepared previously; the methyl^{15b} and benzyl²³ by the oxidation of the corresponding sulfides with chromic acid and the phenyl²⁴ by the reaction of p-nitro-chlorobenzene on benzene sulfinic acid under pressure. The chromic acid method was used in this work.

Ten g. of the sulfide is dissolved in 100 cc. of 80% acetic acid and the mixture heated to boiling, then a saturated solution of chromic acid in water is added a little at a time until an orange coloration denotes the presence of an excess. After boiling for 15 minutes, an equal volume of water is added and the solution allowed to cool. The sulfone separates and is recrystallized from 50% acetic acid to remove chromium compounds. The sulfones are obtained as white plates or needles which are recrystallized to constant melting point.

The sulfones are white solids, crystallizing very well from acetic acid or alcohol. They are very stable towards oxidizing agents, as none of them

²³ Ref. 15a, p. 2270. Ref. 15b.

²⁴ Ullmann and Posdermadjian, Ber., 34, 1154 (1901).

shows any tendency to break at the sulfur atom forming sulfonic acids. The oxidation with chromic acid is exothermic; at the same time the product is purified by oxidation of any disulfides present to soluble sulfonic acids. The sulfones with low melting points separate from the oxidizing mixture as oils but solidify after standing for several hours. The yields are about 85%.

Details of the preparations are given in Table III together with properties of the products. The analyses were made by the method of Parr.

Table III

Preparation and Properties of para-Nitrophenyl Alkyl or Aryl Sulfones,
NO°C*H*SO*R

					Sulfur		
Alkyl or	Nitro	Yiel		M. p.	Cale.	Found	
aryl	sulfide	G.	%	° C.	%	%	Form
Methyl ^a	10	10	84	142.5	15.97	16.02	Needles
Ethyl	. 10	9	76	138.5	14.91	14.98	Plates
isoPropyl	. 8	8	86	115.3	14.01	14.41	Plates
Propyl	. 10	10	86	114	14.01	14.32	Plates
isoButyl	. 10	10	87	73	13.20	13.25	Needles
Butyl	. 15	12	70	56.4	13.20	13.28	Plates
isoAmyl	. 15	12	70	62.5	12.49	12.55	Plates
Phenyl ^a	22.5	22.5	88	142			Plates
Benzyl ^a	. 5	5.5	97	172			Plates

 $[^]a$ Prepared by other authors who give the melting point of the methyl as 136°, the phenyl 143°, and the benzyl 169°.

(d) Alkyl and Aryl para-Aminophenyl Sulfones, RSO₂C₆H₄NH₂

Two of this series of amino sulfones have been prepared previously, the methyl^{15b} and phenyl²⁵ derivatives by the reduction of the nitro bodies with tin and hydrochloric acid.

We have prepared others by reduction from the corresponding nitro compounds described above.

Five g. of the nitrophenyl sulfides. When the reduction is finished the charge is diluted with two volumes of water, heated to boiling and filtered hot. In the case of the first 7 products, the iron residue is extracted twice more with 500 cc. of hot water, but with the last two alcohol is used, since they are not very soluble in water. The water or alcohol extracts are cooled to 0° , at which a large percentage of the product crystallizes; but in the case of the methyl and ethyl derivatives it is necessary to evaporate to a small volume before any solid is obtained. The yields are about 90%, being low in the case of the methyl and ethyl compounds on account of their greater solubility.

The amino sulfones are white, odorless solids, and are much more soluble than the corresponding amino sulfides, the solubility decreasing with increase in the size of the radical. The first 4 numbers of the series melt lower than the corresponding nitro compounds while the last 5 melt higher. The methyl and ethyl compounds darken considerably on standing in light and air but the others remain white.

²⁵ Ref. 24, p. 1155.

Details of the preparations are given in Table IV.

TABLE IV

PREPARATION AND PROPERTIES OF para-Aminophenyl Alkyl or Aryl Sulfones, RSO₂C₆H₄NH₂

	Nitro				Suli	ur	
Alkyl or aryl	sulfone G.	G.	Yield— %	M. p. ° C.	Cale.	Found %	Form
Methyl ^a	. 10	6	70	133	18.74	19.13	Plates
Ethyl	. 10	4	46	89.3	17.33	17.29	Plates
isoPropyl	. 10	7	80	122	16.10	16.29	Needles
Propyl	. 15	12	92	97	16.10	16.37	Needles
isoButyl	. 10	8	91	83.7	15.06	15.52	Plates
Butyl	. 10	8	91	109	15.06	15.28	Needles
isoAmyl	. 11	9	92	110	14.12	13.97	Needles
Phenyl ^a	. 10	8	90	176			
Benzyl	. 5	4	89	218.5	12.99	13.11	Needles

^a Prepared by other authors who give the melting point of the methyl as 137°, and the phenyl 176°.

II. (a) Alkyl and Aryl para-Nitrobenzyl Sulfides, NO₂C₆H₄CH₂SR

No para derivatives of this class have been made though $ortho^{26}$ and $meta^{27}$ nitrobenzyl-methyl sulfides have been prepared and also the corresponding amines. In these cases the sodium salt of the nitrobenzyl mercaptan was used with methyl iodide. As the para mercaptan is rather difficult to prepare, it was thought that the para sulfide could be obtained by the reaction of p-nitrobenzyl bromide on the sodium salt of the various mercaptans.

The methyl and ethyl derivatives could not be prepared in this way as, on adding a solution of the theoretical quantity of sodium ethylate saturated with an excess of the mercaptans to p-nitrobenzyl bromide, p,p'-dinitro-dibenzyl sulfide, ²⁹ m. p., 159°, resulted, though the butyl, *iso* amyl and phenyl derivatives were thus obtained, using the mercaptans.

One-tenth g.-mole of p-nitrobenzyl bromide is dissolved in 100 cc. of alcohol and heated to 60°. To this is added 0.1 mole of sodium mercaptide made by adding an alcohol solution of 0.1 mole of sodium ethylate to the mercaptan. This is added slowly with rapid agitation at 60° and after 15 minutes the alcohol is distilled and the excess of mercaptan distilled with steam. The oil is washed with water and dried with calcium chloride. In the case of the phenyl compound which is solid it is recrystallized from alcohol. Details are given in Table V.

The mercaptan salt has no apparent reducing action on the nitro group when p-nitrobenzyl bromide is still present in excess, but beyond this point it reduces the sulfide to a red substance which is probably an azo compound. Excess of the free mercaptan has no effect, the sodium salt being

²⁶ Gabriel and Stelzner, Ber., 29, 163 (1896).

²⁷ Lutter, Ber., 30, 1070 (1897); m. p., 31°.

²⁸ Waters, Inaug. Dissertation, Munich (1905).

²⁹ Otto Fischer, Ber., 28, 1337 (1895).

necessary for the reduction. The reaction seems best at $60-70^{\circ}$, for at room temperature the *p*-nitrobenzyl bromide is rather insoluble in alcohol. The phenyl compound is solid and may be purified by crystallization from alcohol or acetic acid. The butyl and *iso* amyl derivatives are

TABLE V

Preparation and Properties of para-Nitrobenzyl Alkyl or Aryl Sulfides, $NO_2C_6H_4CH_2SR$

Alkyl		•					Sulfur			
or aryl	G.	RSH G.	Na G.	G. Yi	eld—	М.р. °С.	d_{25}^{25}	Calc.	Found $\%$	Form
Butyl	77.7	43.2	8.28	62	76.6		1.1462	14.25		Oil
isoAmyl	32.4	16.2	3.45	33.7	94		1.1513	13.41		Oil
Phenyl	17.2	8.8	1.84	14.5	74.3	79		13.10	13.26	White plates

higher-boiling oils which decompose on distillation at 5 mm. pressures. They have an odor similar to the corresponding oils in the previous series. The yields are about 75%.

(b) Alkyl and Aryl p-Aminobenzyl Sulfides, NH2C6H4CH2SR

These compounds are prepared in the same way as the amino sulfides of the previous series, and resemble them in properties, the phenyl compound being solid also, but having a lower melting point. The oils were isolated as the slightly soluble sulfates which were recrystallized to remove *p*-aminobenzoic acid.

TABLE VI

Preparation and Properties of para-Aminobenzyl Alkyl or Aryl Sulfides, $\mathrm{NH_2C_6H_4CH_2SR}$

Alkyl	Nitro					Sul	fur ^a
or aryl	sulfide G.	G.Yi	eld— %	М. р. ° С.	d ₂₅	Cale.	Found %
Butyl	13	10	89		1.0321	6.66	6.75
isoAmyl	10	8	41		1.0307	6.20	6.28
Phenyl	7.25	6	94	72		14.91	35.13

^a The first two of the series are oils, and the analyses were therefore made on the sulfates of the bases, only the sulfur in the sulfate ion being determined. These sulfates are obtained as curdy precipitates, very slightly soluble in cold water, something like 1 g. per liter. On recrystallization from hot water, they separate in flocculent form.

(c) Alkyl and Aryl para-Nitrobenzyl Sulfones

The sulfones of this class are prepared in the same way as those of the previous series. They are crystalline solids, and are formed with a good yield,—about 75%. The butyl and isoamyl compounds are contaminated with 5–10% of p-nitrobenzoic acid, which lowers their melting points and which it is practically impossible to eliminate by crystallization. It is removed by agitating several times with a large volume of 5% solution of sodium carbonate. The sulfones may be recrystallized from acetic acid or alcohol. They are very slightly soluble in water; when the oxidation is carried out with a water suspension of the sulfide a poor yield of sulfone

Phenyl.....

contaminated with tar is obtained. Hot 20% sodium hydroxide solution decomposes the sulfones, giving a red solution and a yellow precipitate (m. p., 195°) which contains no sulfur and is probably a compound of the formula $\mathrm{NO_2C_6H_4CH:CHC_6H_4NO_2}$ (m. p., $210\text{--}216^\circ$).

A similar decomposition³⁰ has been noted with sulfone esters.

Table VII

Preparation and Properties of para-Nitrobenzyl Alkyl or Aryl Sulfones,

209.5

11.58

11.51

Plates

	Nitro			Sulfur					
Alkyl or aryl	sulfide G.		ld——	М. р. ° С.	Cale.	Found	Form		
Butyl	33	19	50	139.5	12.49	12.40	Plates		
isoAmyl	36.5	31	75	117	11.83	11.81	Plates		

7.2

NO.C.H.CH.SO.R

(d) Alkyl and Aryl para-Aminobenzyl Sulfones, NH2C6H4CH2SO2R

The amino sulfones are prepared in the same way as those of the former series, starting with material free from p-nitrobenzoic acid, and have similar properties. They are removed from the iron residue by extraction with alcohol. They were recrystallized by dissolving in hot alcohol, adding water cautiously to incipient separation and cooling.

Table VIII Preparation and Properties of Alkyl or Aryl para-Aminobenzyl Sulfones, NH $_2$ C $_6$ H $_4$ CH $_2$ SO $_2$ R

	Nitro			Sul	fur	
Alkyl or aryl	sulfone G.	G. %	М. р. °С.	Calc.	Found %	Form
Butyl	8	6 - 85	95	14.11	13.9	Needles
isoAmyl	11	7 71	126	13.30	13.32	Needles
Phenyl	7.2	4 62	180	13.00	13.20	Needles

III. (a) p,p'-Dinitro-diphenyl Derivatives with Various Groups between the Two Rings, NO₂C₆H₄.X.C₆H₄NH₂

In this series of compounds, p,p'-dinitro-diphenyl may be considered the simplest member, the more complicated ones consisting of various radicals containing sulfur between the two rings, X in the above formula standing for the following groups: $-S-, -CH_2S-, -CH_2SCH_2-, -SC_2H_4S-, -SC_2H_4S-, -SC_2H_4SC_2+, -SC_2H_4SC_2-, -SC_2H_4S-$

Nietzki and Bothof³² prepared dinitro-diphenyl sulfide by treating p-nitro-chlorobenzene with sodium sulfide. This reaction was rather slow and did not go to completion. p,p'-Dinitro-benzylphenyl sulfide was formed from p-nitrobenzyl bromide and sodium p-nitro-thiophenol. p,p'-Dinitro-dibenzyl sulfide was prepared by Fischer²⁹ from p-nitrobenzyl chloride and ammonium sulfide. Others of the series containing two or more separated sulfur atoms we obtained from two molecules of sodium p-nitro-thiophenolate with the following halides, methylene iodide, ethyl-

³⁰ Michael and Comey, Am. Chem. J., 5, 349 (1883-84).

ene bromide, trimethylene bromide, benzal chloride, mustard gas and mustard gas sulfone. In all cases the reaction took place at once with the separation of the new compound. Methylene chloride did not react at all because of its low boiling point and the inactivity of the chlorine atoms; hence, the iodide was used. In the case of ethylene bromide the reaction took place on warming to 70°, but when one ethylene hydrogen has been replaced by methyl, as in propylene dibromide, the reaction is much slower and the resulting compound was contaminated with a large amount of disulfide, produced by oxidation of the mercaptan either by the nitro group or by air. This takes place only to a very limited extent when the reaction is rapid. This was borne out by the fact that using butylene dibromide, in which two ethylene hydrogen atoms have been replaced by methyl, the desired reaction was so slow that the product obtained consisted almost entirely of disulfide.

Mustard gas and its sulfone both react immediately with the mercaptide, their chlorine atoms being much more active.

These nitro sulfides are yellowish, odorless solids which crystallize well from acetic acid, and are insoluble in water and only slightly soluble in alcohol. The yields average about 85%.

Inasmuch as the different compounds are made, using several intermediates, and the preparation is self-explanatory from Table IX, following, it will suffice to describe one completely, the others being made in the same way.

One-tenth g.-mole of methylene iodide is dissolved in 100 cc. of alcohol and 0.21 mole of sodium p-nitro-thiophenolate, with enough water to produce a thick paste, is added. The mixture is stirred while being heated on a water-bath to 65–70°. After a few minutes at this temperature, the reaction is complete and the solid sulfide partly precipitates. On cooling to 0°, practically all of the sulfide separates and is filtered off. It is purified by boiling with a 1% sodium carbonate solution and recrystallized from 80% acetic acid in which it is fairly soluble hot, and very slightly so cold; the latter treatment removes any dinitro-diphenyl disulfide formed.

Table IX $Preparation \ and \ Properties \ of \ p,p'-Dinitro-diphenyl, \ Compounds, \ NO_2C_6H_4-X-C_6H_4NO_2$

						Sulf	UI	
\mathbf{x}	Mercaptide G.	Halide G.	G. Yield	1— %	М. р. °С.	Calc.	Found	Properties
—S—a	7.8	31.5	10	36	154			Orange plates
—CH₂S—	17.8	21.6	27.4	94	108	11.07	10.99	Pale yellow plates
$=(\mathrm{CH_2})_2\mathrm{S}^a$	9.6	17.28	11.5	95	159			Yellow needles
-SCH ₂ S-	35.4	26.7	23.5	83	179	19.88	19.83	Olive plates
$-S(CH_2)_2S-$	17.7	9.4	10	60	136	19.06	19.11	Yellow plates
-S(CH ₂) ₃ S	35.4	20.2	32	91	110	18.29	18.33	Yellow plates
-SCH(C6H5)S-	- 35.4	16.1	30	75	150.5	16.09	16.03	Yellow needles
$=(SCH_2CH_2)_2S$	17.7	8	15	76	86.5	24.28	24.29	Yellow plates
$= (SCH_2CH_2)_2SC$	$O_2 = 27.7$	14.5	25	7.7	170	22.48	22.48	Pale yellow plates

^a Previously known, the melting points being given as 154° and 159°, respectively.

(b) p,p'-Diamino-diphenyl Compounds (NH2C6H5)2X

Two amines of this group have been made previously. Nietzki and Bothof^{3a} prepared thio-aniline by reducing the dinitro derivative, while Mertz and Weyth³¹ prepared it by a fusion of aniline with sulfur. O. Fischer³² reduced dinitro-dibenzyl sulfide to the corresponding diamine with tin and hydrochloric acid. We have prepared these and the other amines of this group by reducing the dinitro compounds just described with iron and acetic acid as outlined above. Benzene was used for extracting the amines from the iron residue. On concentrating and cooling the benzene solutions, the amines were usually obtained as crystals. One of them is an oil.

The amines are very slightly soluble in water, more soluble in alcohol and very soluble in benzene. The solubility in all cases decreases rapidly with increase in molecular weight.

Table X Preparation and Properties of p,p'-Diamino-diphenyl Compounds, NH₂C₆H₄—X—C₆H₄NH₂

					Sul	fur	
X	Nitro comp. G.	G. Yi	eld— %	М. р. ° С.	Calc.	Found	Properties
_S_a	0.	٥.	. 70	108	70	70	Needles
—CH ₂ S—	10	6	76	93	13.92	14.10	Flat needles
$=(CH_2)_2S^a$	5.5	3	68	105			White plates
-SCH ₂ S-	10	7.5	92	99	24.43	24.47	Red needles
-S(CH ₂) ₂ S	10	7.25	88	111	23.20	23.28	Red needles
-S(CH2)3S-	5.5	4	87		8.26^{b}	7.97	Oil
$-SCH(C_6H_5)S-$. 10 *	7.5	88	131	18.93	18.40	White needles
$=(SCH_2CH_2)S$	6	4.5	88	93	28.60	28.54	Red needles
$=(SCH_2CH_2)SO_2$	6	5	97	149	26.12	26.22	White needles

 $^{^{\}rm a}$ Previously prepared, the melting points being given as 108° and 105°, respectively.

b In the sulfate ion of the sulfate.

(c) Sulfones from the Dinitro-diphenyl Compounds

Fromm and Wittmann³⁸ prepared dinitro-diphenyl sulfone by oxidizing the sulfide dissolved in acetic acid with chromic acid. Following the procedure described above for preparing mononitro sulfones, we obtained disulfones in all cases except from p,p'-dinitro-diphenyl-dithiomethane, where the two sulfur atoms are separated only by a CH₂ group and oxidation breaks the molecule, yielding only soluble sulfonic acids. Various oxidizing agents were tried with the same result. In the case where the two sulfur atoms were separated by two CH₂ groups, no difficulty was encountered even when three sulfur atoms are present.

The sulfones are insoluble in water, slightly soluble in alcohol, and

³¹ Mertz and Weyth, *Ber.*, **3**, 978 (1870).

³² Ref. 29, p. 1338.

³⁵ Ref. 15a, p. 2270; m. p., 282°.

fairly soluble in boiling 80% acetic acid, the last member, however, being insoluble in this, as the solubility of the series decreases markedly with the increase in molecular weight. They are white solids with high melting points, and are obtained in yields averaging 75%.

Table XI

Preparation and Properties of Sulfones from p,p'-Dinitro-diphenvl Compounds, NO₂C₆H₄.X.C₆H₄NO₂

					Sulfur			
X	Nitrosulfid G.	G. Yiel	d−%	М. р. °С.	Cale.	Found %	Form	
$-SO_2$	12	11	82	282			Needles	
-CH ₂ SO ₂ -	13.7	13.7	90	195	9.95	10.03	Plates	
= (CH2)2SO2	6	5	75	260	9.54	9.49	Needles	
$-SO_2(CH_2)_2SO_2-$	10	9	75	$235~{ m dec}$	16.02	16.16	Needles	
$-SO_2(CH_2)_3SO_2-$	12.5	7	47	208	15.48	15.59	Needles	
$= (SO_2CH_2CH_2)_2SO_2$	12	11	80	235 dec	19.54	19.68	Needles	

(d) Reduction Products of p, p'-Dinitro-diphenyl Sulfones

The preparation of diamino sulfones is much more difficult than that of the mono-amine sulfones in Classes I and II. Fromm and Wittmann³⁴ obtained diamino-diphenyl sulfone by reducing the corresponding nitrosulfone with tin and acid. This reduction also took place with iron and acetic acid but on carrying it to the next member of the series, p,p'-dinitrobenzylphenyl-sulfone, a compound was obtained which seemed by analysis to be a nitro-amino sulfone and could not be reduced further by this means; m. p., 215° (decomp.). Analysis: Calc. for S, 10.98. Found: 11.26. Dinitro-dibenzyl sulfone yielded a white, tarry substance.

These last two reductions were readily effected by using tin and hydrochloric acid in alcohol, the tin double salt separating on cooling. From this the desired base was obtained.

In the case of the di- and tri-sulfones, neither method of reduction was satisfactory. According to the analyses of the compounds isolated, both nitro groups had been reduced, and also one sulfone group to a sulfide; or both sulfone groups to sulfoxide, this being the case with the di- and tri-sulfones. Various methods of reduction were tried but the desired compounds were not obtained; according to the analyses, NO₂C₆H₄SO₂-

Table XII Preparation and Properties of p,p'-Diamino-diphenyl Sulfones, NH2C6H4.X.C6-H4NH2

\mathbf{x}	Nitro compound G.	I — Yield—	M, p,	Sul Calc.	fur Found %	Properties
-SO ₂ -a	4	2.5 78	176.5			Yellow needles
-CH ₂ SO ₂ -	10	7 86	216	12.22	12.28	White plates
$= (CH_2)_2 SO_2$	5	3 73	187.5	11.60	11.91	Yellow needles

a Previously prepared.

³⁴ Ref. 15a, p. 2270; m. p., 174°.

 $C_2H_4SO_2C_6H_4NO_2$ reduced to the compound $NH_2C_6H_4SO_2C_2H_4SC_6H_4NH_2$; calc.: S, 20.75; found, 20.87; m. p., 206° (chars).

Preparation and Application of the Dyes

1. From Mono-amines. See Tables II, IV, VI and VIII

One-hundredth g.-mole of the base (in case it is liquid the equivalent quantity of the sulfate) is dissolved in two equivalents of hydrochloric acid in 75 cc. of water, and diazotized with one equivalent of sodium nitrite at 5° , maintaining an excess of nitrate for a half-hour, as shown by the starch-potassium iodide test. One-hundredth mole of R-salt, plus 5° excess, is dissolved in 50 cc. of water to which have been added two equivalents of sodium carbonate, and the mixture is cooled to 5° . The diazo solution is added to the alkaline solution of R-salt at this temperature, and the whole stirred half an hour. In some cases the dye separates immediately, while in others it remains in solution. At the end of this time a small sample is salted out and spotted on paper, the clear ring being tested with R-salt solution to detect the presence of any diazo body; none should be present, as shown by the absence of color on this ring. The solution should also be alkaline to Brilliant Yellow paper, adjustments being made in cases where it does not answer these requirements. After the coupling is complete the solution is heated to 45° and enough salt is added in small amounts to obtain a clear, or slightly colored, ring when spotted on paper. The dye is filtered out from the warm solution and dried at 80° .

These dyes belong to the class of acid colors, dyeing animal fiber from a weak acid bath, the application being made in the following way. As the strength of the several dyes varies considerably due to the amount of salt present, in order to obtain dyeings of approximately the same strength for comparison, it is necessary to make standard solutions of 500 cc. of 0.1%, of each. These are spotted on paper and the weak and strong ones noted, corrections being made in the volume of solution used for dyeing. For a 2% dyeing on a 10 g. woolen skein, 200 cc. of this solution is used, and more or less is added according to the strength. The measured volume is diluted to 700 cc., 4% sulfuric acid and 15% Glauber's salt, based on the weight of material dyed, being added. The wool which has been thoroughly wet in warm water, is immersed and the whole is heated slowly to boiling, while the skeins are turned frequently to insure even dyeing. After 30 minutes' boiling the bath is exhausted, and the skeins are removed, washed and dried.

Both in the preparation of the dyes and the application, approximately standard solutions of the various acids, bases and salts were used, so that the desired quantities could be easily measured.

In this same manner, dyes were made from thio-anisidine and thio-ansidine sulfone, the following intermediates being used in addition to R-salt: salicylic acid, Schaeffer's salt, Neville and Winther's acid, L-acid, (1-OH, 5-SO₃H) and chromotrope acid. For comparison, the corresponding dyes were prepared from p-toluidine and p-anisidine.

2. From Diamines. See Tables X and XII

One-hundredth g.-mole of the base is dissolved in 100 cc. of hot water containing 0.04 g.-mole of hydrochloric acid, cooled to 5° and diazotized with 0.02 g.-mole of sodium

nitrite, while an excess of nitrite is maintained for one-half hour as shown by the starch-iodide test; 0.022 mole of salicylic acid is dissolved in an equivalent quantity of sodium hydroxide, so that it is just alkaline to Brilliant Yellow paper, and then 0.2 mole of sodium carbonate is added. This solution is cooled to 5° and the tetrazotized base, which has previously been neutralized to a slight acidity to congo red paper, is added slowly at this temperature. After three hours it is tested for excess diazo with R-salt solution, by spotting a sample on paper and testing the clear ring. This should be negative, showing that the first molecule of salicylic acid has coupled; 0.02 moles of sodium hydroxide is added and the temperature brought slowly to 35° , stirring overnight at this temperature. In the morning the second molecule should be coupled, and the solution should be strongly alkaline to Brilliant Yellow paper. To test for excess of the second diazo group, a small amount of color is diluted and divided between two test-tubes, and to one several drops of 1% H-acid solution are added. Both are heated to boiling and should remain the same color. A change in the one containing H-acid denotes the presence of free diazo group. The dyes are heated to 50° and salted out.

Dyes containing salicylic acid are commonly known as acid chrome colors, since the color is fixed on the wool with a dichromate mordant. These colors were dyed as follows.

A standard solution of dye is made as described above, and the quantity measured to give a 2% dyeing; 3% acetic acid and 15% Glauber's salt are added, the skein is immersed and boiled for 1/2 hour. An addition of 3% acetic acid is made and the boiling continued for another half hour. In case the dye is to be chromed, this is followed by adding 10% dichromate and boiling for another half hour, after which the skeins are removed, washed and dried.

Thio-aniline, thio-aniline sulfone and the diamine from mustard gas, NH₂-C₆H₄SCH₂CH₂SCH₂CH₂SC₆H₄NH₂, were tetrazotized and coupled with the other intermediates which were used with the mono-amines described above.

At the same time similar dyes from benzidine itself were prepared for comparison. The couplings were made in the same way as with salicylic acid described above, except that sodium carbonate was substituted for the hydroxide, the couplings being made in a weaker alkaline solution. In this series also the first molecule of intermediate was coupled at a low temperature and, after testing with R-salt for uncombined tetrazo body, the temperature was elevated to 35° and the suspension stirred overnight.

The dyes obtained were applied to wool in exactly the same way as the acid dyes obtained from mono-amine bases.

Additional dyes were made with these same bases by coupling them with intermediates used to produce direct dyes, using naphthionic, gamma-and H-acids. The bases were tetrazotized in the usual way, but the couplings were made in the case of the first two intermediates in neutral solutions, neutrality being maintained during the formation of hydrochloric acid in the course of the coupling; with H-acid the solution was kept alkaline throughout by an excess of carbonate.

These colors are applied to cotton in the following way.

A standard 0.1% solution of the dye is prepared as usual and the required volume for the desired strength is diluted to 250 cc., 15% of sodium chloride, based on the weight of skein used, being added. The skeins are introduced into the boiling solution and allowed to remain there for $^3/_4$ hour and frequently turned.

Colors of the Dyes³⁵

Mono-amine Bases with R-salt. Dyes from Bases of Tables II, IV, VI and VIII

The first study was of the bases in Table II to determine the effect of changing the radical in NH2C6H4SR, R being methyl, ethyl, propyl, isopropyl, butyl, isobutyl, iso-amyl phenyl and benzyl. All of these give red dyes with R-salt, there being no distinguishable difference in color among them except that the -SCH3 is a bordeaux and the -SC6H3 is scarlet. The benzyl group acts exactly like the alkyls higher than the methyl group. The sulfur atom appears here as strongly bathochromic and its influence is so decided that the size or nature of the group beyond it makes little difference; or, what is more probable, the part of the auxochrome group which is in immediate union with the benzene nucleus is the decisive factor. This is shown by a comparison of the isomeric bases containing the groups —SCH₂C₆H₅ and —CH₂SC₆H₅. The dye from the first is deep red, while that from the second is tangerine, the auxochrome effect of the sulfur being lost by the interposition of the -CH₂- group. The same color is shown by the dye from the base containing -CH2SC3H11 (iso). The oxidation of the -S- in these two to $-SO_2$ — has no effect on the color.

Contrasting the amino sulfones of Tables IV and VIII with the amino sulfides of Tables II and VI we find that the oxidation of —S— to —SO₂—destroys the effect of the —S— completely; in fact the sulfone group is actually hypsochromic, the dyes from NH₂C₆H₄SO₂R being gold while the one from aniline itself is orange. The size and character of the radical carried by the sulfone group have no effect on the color, the dyes from all the bases in Table IV being indistinguishable.

A curious fact appears with the dye from $NH_2C_6H_4SCOC_6H_5$. This contains —S— joined to the nucleus and, according to what was said above, was expected to be deep red like the dye from $NH_2C_6H_4SCH_2C_6H_5$ from which it differs only in the oxidation of the — CH_2 —. The dye in question is scarlet but its tinctorial power is so diminished that only a moderate color was obtained by double strength dyeing. Here oxidation, even of a group beyond the sulfur, has lightened the color.

2. Mono-amine Bases with Various Intermediates

As it appears that the alkyl present in the sulfide and sulfones is of little consequence, further comparisons were made between dyes containing the groups $-CH_3$, $-CCH_3$, $-SCH_3$ and $-SO_2CH_3$; that is, p-toluidine, p-anisidine, p-thio-anisidine and its sulfone were diazotized and coupled with salicylic acid, Schaeffer's salt, Neville and Winther's acid, L-acid,

³⁵ Thanks to Dr. R. E. Rose, the color designations here given are from the Technical Laboratory of E. I. du Pont de Nemours and Co.

R-salt and chromotrope acid. The colors of the dyes obtained are given in the table below.

Table XIII
Colors of Dyes from Bases with Various Intermediates

Acids	-СН₃	Auxochromes —OCH ₃	—SCH₃	-SO2CH2
Salicylic	Yellow	Yellow	Yellow, darker	Gold
Salicylic, chromed	Yellow	Yellow	Old gold	Old gold
Schaeffer's	Orange	Scarlet	Red	Gold
Neville and Winther's	Scarlet	Scarlet	Red	Orange
L-acid	Red	Red	Bordeaux	Old gold
R-salt	Scarlet	Red	Bordeaux	Gold
Chromotrope	Cardinal	Heliotrope	Violet	Red

We have here the same color relations, the auxochromes being arranged in the order: $-SCH_3 > -OCH_3 > -CH_3 > -SO_2CH_3$. This is true regardless of the nature of the second constituent of the dye.

3. Diamine Bases with Salicylic Acid, Chromed. See Tables X and XII

The colors obtained are as follows: (1) benzidine, gold; (2) thioaniline, old gold; (3) and (4) the rings joined by -CH2S- and -CH2-SCH₂—, old gold; (5) by —SCH₂S—, old gold but deeper; (6) and (7) by -SCH₂CH₂S- and -SCH₂CH₂SCH₂CH₂S-, gold. The presence of sulfur connected to two rings in thio-aniline darkens the color considerably as compared with benzidine. The introduction of one or two methylene groups with one sulfur atom weakens the coloring property, and the sulfone is still weaker. In the case where two sulfur atoms are separated by CH₂, the color is practically the same as with thio-aniline, the influence of the CH2 being overcome by the relatively large amount of sulfur adjacent. Where the sulfur atoms are farther apart, being separated by ethylene, the color is much lighter and more greenish, lacking the reddish overcast obtained with thio-aniline and its sulfone. Where the two rings are separated by three sulfur atoms and two ethylene groups, the color is still darker and greener, while the introduction of a sulfone group in the center between the two ethylenes does not change the color at all, showing again that the sulfur atoms connected directly to the rings are the ones that exert the most influence on the color.

The sulfone of thio-aniline gives an old gold, the same as thio-aniline but darker apparently reversing the relationship found above between sulfides and sulfones. The dye from mustard gas sulfone is practically the same as that from mustard gas, which is as would be anticipated since the —SO₂— in the group —SCH₂CH₂SO₂CH₂CH₂S— cannot be expected to show much effect.

For these diamines, alicylic acid was used because of the importance of Anthracene Yellow C (Cassella)³⁶ obtained by coupling this inter-

³⁶ Schultz, "Farbstofftabellen," 1914, p. 294.

mediate with thio-aniline. The couplings were made in the following way, as were also the acid colors described subsequently.

4. Diamine Bases with Various Intermediates

The dyes from thio-aniline, thio-aniline sulfone and the diamine from mustard gas when coupled with various intermediates are contrasted with those from benzidine. The colors are given in the following table.

TABLE XIV

Colors of Dyes from	CERTAIN DIAMIN	es Coupled	WITH VARIOUS	Intermediates
Acids	Benzidine	-S	-SO ₂ = (SCH ₂ CH ₂) ₂ S
Salicylic (chromed)	Yellow	Gold	Gold	Yellow
Schaeffer's salt	Maroon	Scarlet	Orange	Scarlet
Neville and Winth	er's Heliotrope	Red	Scarlet	Red
L-acid	Claret	Claret	Burnt orange	Red
R-salt	Purple	Claret	Burnt orange	Red
Chromotrope	Purple	Heliotrope	Claret	Heliotrope
Gamma-acid	Violet	Claret	Claret	Red
Chicago acid	Purple	Lilac	Maroon	Violet
H-acid	Blue	Purple	Maroon	Lilac

This series of colors indicates that where the diphenyl rings are separated by sulfur, sulfone and other groups, they no longer possess the properties of benzidine, which gives colors varying from deep reds to blues and violets. The thio-aniline and its sulfone give much lighter colors, differing slightly but practically in the same range of the spectrum as those obtained from the mono-amines coupled with the same acids, though the molecular weight is greater than that of the benzidine dyes and approximately double that of the mono-amine series. The dyes containing three sulfur atoms, with the mustard gas residue between, are also slightly lighter than those from thio-aniline.

In this series the sulfur divides the molecules, so that the colors obtained appear as if each half were acting as a unit, while with benzidine the effect of each group is felt in the opposite ring.

The three diamine bases having —SCH₂S—, —SCH₂CH₂S— and —SCH₂CH₂CH₂S— between the rings were coupled with gamma-acid. The dyes from the first two were red and practically identical, but the last gave a maroon.

The conclusion drawn above, that these diamine bases do not possess the properties of benzidine, is borne out by the fact that they do not form direct cotton dyes. Benzidine, coupled with gamma-acid or H-acid, forms colors which dye cotton direct from a salt bath. Those obtained from the three sulfide bases used in the previous series, when coupled with intermediates suitable for producing direct colors, are found to be lacking in this property. The benzidine dyes exhaust the bath completely, while the others do so only in part; some color, however, remains in the fibre. The

dyes from the trisulfide bases from mustard gas show some tendency towards being direct, as the colors do not wash out in cold water. The monosulfides are poorer, and in the case of the sulfones practically all of the color washes out in cold water. On the other hand, all of them are removed in boiling water.

Table XV gives the colors of these dyes on cotton. Here also the color effect produced by the sulfide and sulfone groups is the same as with the acid dyes described above.

TABLE XV

COLORS OF DYES FROM DIAMINE BASES COUPLED WITH SEVERAL INTERMEDIATES AND Dyed over Cotton

Intermediates	Benzidine	—S—	-SO ₂ =	(SCH ₂ CH ₂) ₂ S
Naphthionic acid	Red	Burnt orange	Burnt orange	Gold
Gamma-acid	Violet	Claret	Claret	Maroon
H-acid	Blue	Blue	Lilac	Violet

Summary

A series of bases, p-NH₂C₆H₄SR, has been made and these have been diazotized and coupled with R-salt to find the effect of changes in the radical R on the color. Dyes have been made from p-toluidine, p-anisidine, p-thioanisidine and its sulfone by diazotizing and coupling with a number of intermediates. It has been found that -SCH₃ > -OCH₃ > -CH₃ > -SO₂CH₃ act as auxochromes.

Diamine bases of the type ρ, ρ' -NH₂C₆H₄-X-C₆H₄NH₂ have been made in which X is -S-, -SO₂-, -SCH₂-, -SCH₂S-, -SCH₂CH₂S-, -SCH₂CH₂SCH₂CH₂S-, etc., and these were tetrazotized and coupled with various intermediates to find the effect of the group between the two rings on the color of the dves. These bases do not resemble benzidine in giving fast cotton dyes.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

ARYL 1,3-BENZO-DIOXANES (ARYL METHYLENE-SALIGENINS)

By Roger Adams, A. W. Sloan and B. S. Taylor RECEIVED JUNE 11, 1923

In a contribution from this Laboratory on the structure of disalicyl aldehyde,1 it was shown that saligenin condensed readily with benzaldehyde to yield 2-phenyl-1,3-benzo-dioxane according to the following equation.

$$\begin{array}{ccc}
CH_2OH & + C_6H_5CHO \longrightarrow & & & \\
OH & & \\
OH$$

¹ Adams, Fogler and Kreger, This Journal, 44, 1126 (1922).

Since a condensation of this type has not been previously described a study has been made of the condensation of certain substituted benzaldehydes with saligenin and substituted saligenins. It has been found that the reaction is quite general and takes place with the greatest ease. Whereas it was necessary to have present a catalyst, such as a small amount of benzoic acid, when benzaldehyde condensed with saligenin, no catalyst was found necessary with the substituted compounds. Cinnamic aldehyde condensed like the aromatic aldehydes and it is probable that any α,β -unsaturated aldehyde will react similarly. Simple aliphatic aldehydes did not condense with saligenin to give dioxanes under similar conditions

The condensation to form dioxanes is a type of acetal formation and resembles the condensation of benzaldehyde with trimethylene glycol² or trimethylene glycol derivatives. The only difference is that in saligenin one of the hydroxyl groups is a phenol and the other is an alcohol. Since it has been shown that aromatic aldehydes form acetals with phenols under proper conditions, and these are intermediates in the formation of triphenyl methane compounds, it is not surprising that aromatic aldehydes condense with saligenin to form dioxanes. Apparently there is no tendency for the products formed to rearrange into triphenyl methane or analogous compounds.

The 2-aryl-1,3-benzo-dioxanes are formed in very good yields (60–95%). They are white crystalline compounds and, like simple acetals, very stable toward alkalies but unstable toward acids, with the formation of saligenin and aldehyde.

Experimental Part

General Method for the Preparation of 1,3-Benzo-dioxanes.—A mixture of 1 molecular equivalent of saligenin or substituted saligenin and benzaldehyde or substituted benzaldehyde was heated on a steam-bath until a homogeneous liquid resulted. This required generally 5 to 30 minutes but in the case of nitrobenzaldehyde and saligenin, almost 2 hours. After the heating, the reaction mixtures were allowed to stand at room temperature until they solidified, the time required varying from a few minutes to 8 to 10 hours. The resulting solids were washed with water and crystallized from alcohol. In the cases of benzaldehyde and saligenin and nitrobenzaldehyde and saligenin, benzoic acid was used as a catalyst. In these latter experiments, consequently, the reaction mixtures were washed with sodium carbonate and then with water before crystallization was attempted.

The condensation of nitrosaligenin with benzaldehyde and substituted benzaldehyde was attempted. No definite condensation products could be isolated and in one case apparently no reaction took place.

² Fischer, Ber., 27, 1537 (1896).

1,3-Benzo-dioxanes

Condensed products	M. p.	Analyses
1. Saligenin	107-107.5	Subs., 0.1303: CO ₂ , 0.3247; H ₂ O,
p-Chlorobenzaldehyde	201 20110	0.0058. Calc. for C ₁₄ H ₁₁ O ₂ CI: C,
		68.15; H. 4.46. Found: C. 67.96;
		H, 4.43.
2. Saligenin	117-117.5	Subs., 0.1183: CO ₂ , 0.2507; H ₂ O,
p-Bromobenzaldehyde		0.0043. Cale. for C14H11O2Br: C,
		57.73; H, 3.78. Found: C, 57.79;
		H, 3.68.
3. Saligenin	88-89.5	Subs., 0.1815: N ₂ (corr.), 15.45 cc.
m-Nitrobenzaldehyde		Calc. for $C_{14}H_{11}O_4N$: N, 5.45.
		Found: 5.32.
4. Bromosaligenin	S5	Subs., 0.5000: CO ₂ , 650.1 cc. (31.5°,
$5-(Br)-2-(HO)C_6H_4CH_2OH$		741 mm.). Calc. for C ₁₄ H ₁₁ O ₂ Br:
Benzaldehyde		C, 57.73. Found: 58.00.
5. Bromosaligenin	147-148	Subs., 0.5000: CO ₂ , 584.4 ec. (32.5°,
p-Chlorobenzaldehyde		741 mm.). Calc. for C ₁₄ H ₁₀ O ₂ Br-
		Cl: C, 51.62. Found: 51.82.
6. Bromosaligenin	143-144	Subs., 0.5000: CO ₂ , 506.8 cc. (31.5°,
$p ext{-Bromobenzaldehyde}$		739 mm.). Calc. for C ₁₄ H ₁₀ O ₂ Br ₂ :
7 B	118-120	C, 45.42. Found: 45.04.
7. Bromosaligenin Cinnamic aldehyde	118-120	Subs., 0.4000: CO ₂ , 537.2 ec. (29.3°, 741 mm.). Calc. for C ₁₆ H ₁₃ O ₂ Br:
Cimianne aidenyde		C, 60.57. Found: 60.75.
8. Methyl saligenin	90	Subs., 0.2000: CO ₂ , 338.0 ec. (22.5°,
5-(CH ₃)-2-(HO)C ₆ H ₄ CH ₂ OH		743 mm.). Calc. for C ₁₅ H ₁₄ O ₂ :
Benzaldehyde		C, 79.64. Found: 79.59.
9. Methyl saligenin	130	Subs., 0.2000: AgBr, 0.1221. Cale.
p-Bromobenzaldehyde	200	for $C_{15}H_{13}O_2Br$: Br, 26.22. Found:
r — managarang ta		25.97.

Cinnamic aldehyde and saligenin did not give a solid product.

Formaldehyde, acetaldehyde and butyraldehyde were condensed in succession with saligenin but in no case was a dioxan obtained.

Saligenin.—Saligenin was prepared by the reduction of salicyl aldehyde according to the method of Voorhees and Adams.³

Bromosaligenin,⁴ 5-Br-2-HOC₆H₄CH₂OH.—Bromosaligenin was prepared by a slight modification of the method of Auwers.

A solution was made of 50 g. (1 molecular equivalent) of saligenin in 2.5 liters of water in a 12-liter flask. This solution was cooled to $5-10^{\circ}$ and kept cold and stirred mechanically during the addition of 9 liters of bromine water containing 65 g. (1 molecular equivalent) of bromine, requiring about 2 hours. The solution was filtered to remove a small amount of tar and was then extracted with 3 to 4 liters of ether. After the ether had been dried it was distilled and a yellow liquid remained which solidified as it cooled. After crystallization from benzene there was obtained 44 g. of white plates which after a

³ Voorhees and Adams, This Journal, 44, 1397 (1922). See also Carothers and Adams, *ibid.*, 45, 1071 (1923).

⁴ Auwers and Büttner, Ann., 302, 131, 138 (1898).

second crystallization melted at 107-109°. This was used in the condensation mentioned above.

p-Homosaligenin, 5-CH₃-2-HOC₆H₄CH₂OH.—Homosaligenin is difficult to prepare by any of the methods now described in the literature. The best two are treating p-cresol with formaldehyde, and the reduction of homosalicylaldehyde with sodium amalgam. A most satisfactory method was reduction of homosalicylaldehyde with hydrogen and platinum oxide according to the general method described by Carothers and Adams.⁵

A solution of 27.2 g. of p-homosalicylaldehyde in 100 cc. of alcohol was treated with 0.23 g. of platinum oxide and 0.1 cc. of N ferrous chloride solution. The mixture was reduced in the usual way, the time required being about 40 minutes when the hydrogen was passed in under a pressure of about 1.5 atmospheres. The yield was quantitative. The platinum was filtered off, the solution was evaporated and the product recrystallized. It then melted at $105\,^{\circ}$.

Summary

- 1. It has been found that benzaldehyde and substituted benzaldehydes condense with saligenin and substituted saligenins to yield 2-aryl-1,3-benzo-dioxanes.
- 2. The condensations take place with the greatest ease and generally without the addition of a catalyst. In the case of benzaldehyde and saligenin, and of nitrobenzaldehyde and saligenin the presence of benzoic acid greatly speeded up the reaction and gave the best results.

URBANA, ILLINOIS

[Contribution from the Color Laboratory, Bureau of Chemistry, United States Department of Agriculture, No. 81]

PROPERTIES OF DYED MATERIALS

By H. WALES

RECEIVED JUNE 30, 1923

Absorption Spectrum and Its Relationship to Color

Ever since the discovery of artificial colors, attempts have been made to find some relationship between the color and the chemical constitution. For some classes of dyes theories have been worked out with fair success. In practically every case, however, the "color" has been determined by means of the position of the absorption band or bands as determined with a spectroscope.

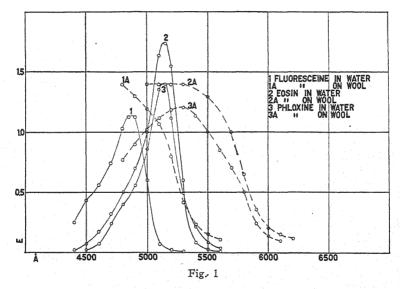
The author has been led to believe by some recent observations that this method is incorrect and that the location of the absorption maximum

⁵ Carothers and Adams, This Journal, 45, 1071 (1923).

¹ Ley, "Beziehungen zwischen Farbe und Konstitution," F. Hirzel, Leipsig, 1911. Watson, "Color in Relation to Chemical Constitution," Longmans, Green and Co., 1918.

or width of the absorption band as ordinarily determined has only a general influence on the color, that is, it will determine whether the color will be red or blue, but will not indicate the particular shade of red or blue. This fact was first brought out through solutions of Formyl Violet S4B and Acid Violet 4B Extra. The second solution was of a decidedly redder cast than the first, although it actually absorbed more red light, there being a shift in the absorption maximum of about 250 Å. towards the red end of the spectrum. Wool dyeings made from these two dyes showed the same color differences as the solutions.

Solutions of the majority of the dyes show broad absorption bands with indistinct maxima, due probably to isomers and subsidiary dyes. The yellows, browns, and most of the oranges are unsuited for spectroscopic work because their absorption is either in the ultraviolet or too



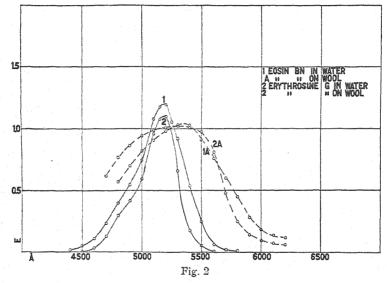
far into the violet to be read with any degree of accuracy. On the other hand, the dyes of the xanthene group show narrow, well-defined bands which fall near the center of the visual spectrum where the accuracy of reading is at the highest. Strangely enough, the one yellow dye of this group, fluoresceine, has its absorption maximum at about 4850 Å. and should therefore, by comparison with other dyes showing similar absorption, be orange-red.²

Since the matching of shades of color is at best subject to large personal errors due to the varying sensitivity of the eye in different individuals, a more absolute method had to be devised. It was found that the ab-

 $^{^{2}}$ The absorption maximum for Orange I is at 4750 Å, and for Ponceau 2 G at 4900 Å.

sorption spectra of wool dyed with different colors differed considerably from those determined from the solutions and offered at least a partial explanation for the color of the cloth.

The method used in this work was similar to that used by Meek and Watson.³ An attachment was fitted to the front of the photometer box of a Hilger spectrometer equipped with a Nutting photometer, to hold the cloth at an angle of 45° with the optical axis of the machine. By means of a suitable source of illumination, light was reflected from the dyed sample⁴ into one orifice of the photometer and from an undyed sample into the other orifice. A depth of dyeing sufficient to show an extinction coefficient of 1.0 to 1.5 was used in every case. This gave colorings of



almost equal intensity from dyes of different tinctorial strengths. Readings made on dyeings of different depths gave curves which were multiples of one another, although in many cases the samples would appear as entirely different shades to the eye. This is undoubtedly due to the varying sensitivity of the eye towards light of different wave lengths. The large amount of "white" light reflected from the surface of the cloth made it impossible to determine whether Beer's law held in this case.

The 17 dyes used in this work are listed in Table I. The absorption maxima were determined to the nearest 25 Å. for solutions and to the nearest 50 Å. for dyeings.

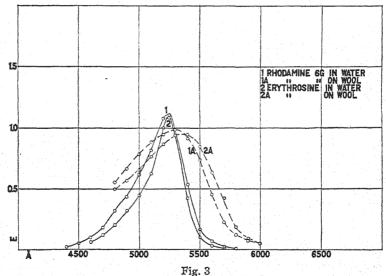
- ³ Meek and Watson, J. Chem. Soc., 109, 545 (1916).
- ⁴ All dyes used in this work were carefully purified and dyeings were made from aqueous solutions containing only the dye.
- ⁶ Compare Luckiesh, "Color and Its Applications," D. Van Nostrand Co., 1915, p. 11, on the effect of illumination.

TABLE I

	@	ABS	SORPTION MAX	IIMA OF	DYES		5
Schu No.		Absorption maximum of aqueous solution Å.	Absorption maximum of wool dyeing Å.	Schult: No.	z ^e Dye	Absorption maximum of aqueous solution Å.	Absorption maximum of wool dyeing Å.
585	Fluoresceine ^a	4875	About 4700	582	Violamine Re	5300	5400
596	Phloxine ^b	5150 -	5300	593	Phloxine P°	5300	5450
587	Eosin^b	5150	About 5100	570	Rhodamine So	5400	5400 +
590	Erythrosine G ^c	5200 -	5300	597	Rose Bengal 3	B° 5400+	· 5600 —
591	Eosine B N ^d	5200	5350	580	Violamine B ^e	5450	5550
583	Violamine G ^e	5225	5350	595	Rose Bengal ^a	5450	5600 —
571	Rhodamine 6 Ge	5250 -	5300	572	Rhodamine G	5500	5400 +
592	Erythrosine ^f	5250	5375	573	Rhodamine B	5550	5500
574	Rhodamine 3 B°	5275	5400				

Makers: "Berlin; "Schöllkopf; "Badische; "Heller; "Höchst; "National aniline; "Bayer.

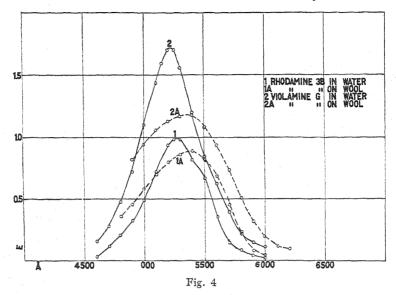
Eight of these dyes, Rhodamine 3B, Rhodamine 6G, Violamine G, Violamine R, Eosin BN, Erythrosine, Erythrosine G and Phloxine P, show absorption maxima in aqueous solutions at 5300 to 5200 Å. Disregarding the fluorescence, dilute solutions of 6 of these appear almost



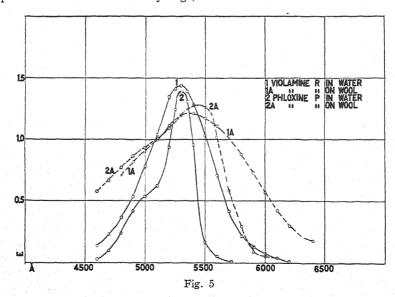
identical in color. Rhodamine 6G is slightly more yellow than these 6, while Violamine R, which shows practically the same absorption as Phloxine P, is decidedly purple. When dyeings are made from these 8 compounds, the series shows a gradual change in tint from a yellow-red to a blue-red. Violamine R still has the deepest color, but the yellowest shade is shown not by Rhodamine 6G but by Erythrosine G.

⁶ Schultz, "Farbstofftabellen," Weidmannsche Buchhandlung, 1914.

An analysis of the curves for the dyed samples shows that the complete curve and not the maximum determines the color. Erythrosine G and



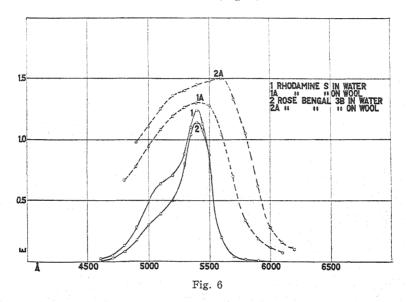
Eosin BN (Fig. 2) show maxima at practically the same point in both their aqueous solutions and wool dyeings, as do also Violamine R and Phloxine



P (Fig. 5). The first two show the same red absorption and the latter two the same blue absorption. Eosin BN, however, transmits more

blue light than Erythrosine G and is therefore bluer. In the same manner, the color of Violamine R is bluer than that of Phloxine P because it absorbs more light towards the red end of the spectrum.⁷

As was mentioned above, Acid Violet 4B extra has a much redder color than Formyl Violet S4B, although it shows a greater absorption in the red region. It also shows slightly more absorption in the blue but not enough to overbalance that in the red. Dyed samples show the same red absorption for both and a greater blue absorption for Acid Violet 4B Extra which is the redder of the two (Fig. 9).



The curves from the dyed samples show to a certain extent the color of an object. The spectrum of a solution will show only whether a dye should be red or blue. Anyone unfamiliar with the color of this solution would be unable to tell whether the unknown was lighter or darker in hue, by comparing its absorption curve with the spectrum of a known color giving a similar curve. Possibly either the absorption in the ultraviolet or in the infra-red or both may have some influence on the color sensation which is received by the eye. At present there are insufficient data on which to base any definite conclusions. A number of dyes have been studied to a limited extent in the ultraviolet, while only those used for sensitizing photographic plates have been examined for transmission in the infra-red.

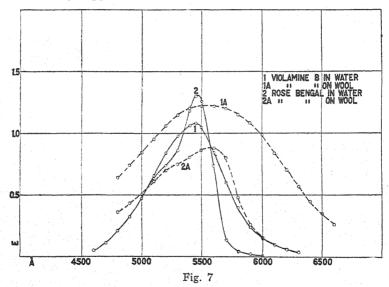
⁷ It is of interest to note that wool stained with alcoholic solutions of the color acids of these dyes gave curves identical with samples dyed from the salts.

^{*} Uhler and Wood, "Atlas of Absorption Spectra," Carnegie Inst. Washington, 1907.

The Mechanism of Dyeing

The older mechanical, chemical and solution theories of dyeing have of late been largely supplanted by the theory of colloidal adsorption by the fiber. The various methods which have been used to demonstrate these theories are incapable of direct proof. For this reason it was thought that a comparative spectroscopic investigation of dyes, both in solution and on the fiber, might shed some light on the subject.

Many investigators have noted that a dye will not show exactly the same absorption of light in two different solvents. Usually both the position of the maximum and the width of the band are altered with a change in solvent. It has also been claimed that the bands become wider as the dye approaches the colloidal condition. On the other hand,



the width of curves obtained from dye lakes¹¹ may or may not be different from those given by the corresponding dyes in aqueous solutions.

The spectrophotometric curves obtained from wool dyeings shown above are much broader than those from the aqueous or alcoholic solutions. When filter paper was stained with any of the xanthene dyes and examined by means of the spectroscope, absorption curves which were identical with those from wool dyeings were obtained, showing that the color is present on both fibers in the same state. Further experiments were made by depositing thin gelatin films of Eosin BN and Erythrosine on glass plates and measuring both the transmission and reflection spectra.

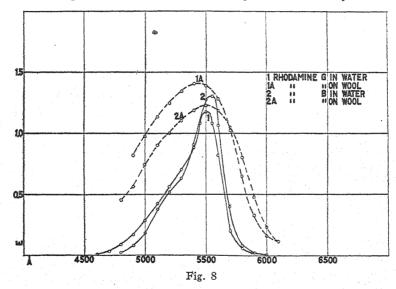
⁹ Bancroft, J. Phys. Chem., 18, 1, 118, 385 (1914); 19, 50, 145 (1915).

¹⁰ Shephard, Proc. Roy. Soc. London, 82A, 245 (1909).

¹¹ Holmes, Color Trade J., 13, 8 (1923).

In both cases the reflection spectra corresponded to those of the wool dyeings and the transmission spectra to those of the aqueous solutions, showing a slight shift in the maxima caused by a change in solvent (Fig. 10). Similar curves were obtained from a film of Erythrosine in cellulose acetate. These results indicate that these dyes are actually dissolved in the wool.

The objections to the solution theory¹² of dyeing are based mainly on the fact that the law of distribution between the solvent and fiber is not followed. Many dyeings are non-reversible.¹³ These objections, as well as most of the proofs put forth to substantiate the various theories, are based on the idea that dyes should act like inorganic or simple organic compounds in solutions. Since dyes do not obey the solution laws when dissolved in liquids, there is no reason to expect them to obey these laws



when dissolved in solids. For example, many sulfonated azo dyes can be completely extracted from aqueous solution by diluting with an equal volume of hydrochloric acid and shaking out with amyl alcohol. Repeated washings with 1:1 hydrochloric acid will not remove any of the dye from the amyl alcohol although the dye is very soluble in hydrochloric acid. When, however, the acidity of this amyl alcohol solution is reduced to below $0.7\ N$ by washing with dil. acid or with water, these dyes return to the aqueous layer. In this and many similar cases dyes show no distribution between two solvents. Under certain conditions the dye

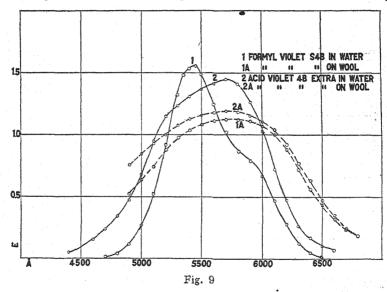
¹² Witt, Färbenztg., 1890-1891, 1.

¹³ Von Georgievics, Mitt. Tech. Gew. Museum Wien, 4, 205, 349; Z. angew. Chem., 16, 574 (1902).

¹⁴ U. S. Dept. Agr., Bull., 448, 12-13 (1917).

will go completely into one solvent and under slightly changed conditions into the other solvent.

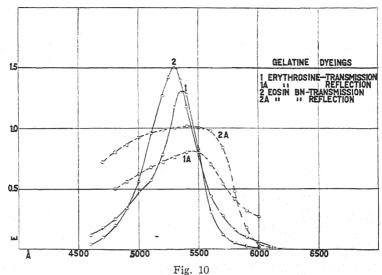
This failure to obey the solution laws may be due to the fact that most dyes are on the border line between the crystalloid and colloid states. This may be shown by some experiments which were conducted on the solubility of pure Tartrazine in water. If Tartrazine and water were placed in a thermostat and solution effected at the desired temperature, good checks on the solubility could be obtained. On the other hand, if solution of an excess of this dye was accomplished at a higher temperature, and then placed in the thermostat, precipitation would not always take place. In fact, many times the solution would continue to dissolve a large additional amount of Tartrazine at this lower temperature until finally some sort of a change in state would take place and an enormous amount of pre-



cipitation would occur. An entirely different value for the solubility of Tartrazine in water was given by this method from that found by the method first described. Many unexpected effects, due to the addition of slight amounts of sodium chloride, were also noticed and will be discussed in a later paper.

The properties of the dye and the fiber are such that a large and probably varying amount of dye would be adsorbed on the fiber in addition to that dissolved by it. For this reason it is extremely doubtful whether it will ever be possible to demonstrate the mechanism of dyeing satisfactorily by the methods which have been used in the past. A practice which cannot be too severely condemned in work of this nature is that of dyeing from solutions containing salts, acids or other leveling agents or assistants which

may cause secondary reactions on the fiber. Unfortunately, this point has been ignored by most investigators. A study of the literature yields a long record of tests made from solutions containing salt, Glauber's salt, sulfuric acid, soap, etc., and on samples which have been treated with various mordants. Attempts have been made to draw conclusions from the results thus obtained before the process of dyeing from solutions



containing only the pure dye has been fully studied. It would seem to be more scientific to investigate first the simple case where dye, fiber and solvent are the only factors concerned. After this has been done, the study of the effect of salt, etc., would follow.

The colloidal adsorption of dyes by the fiber has been successfully demonstrated by Bancroft¹⁶ and others, but most of the work shows that this cannot be the whole of the dyeing process. Some samples of paper pulp¹⁷ were dyed with Pontamine Sky Blue 3BX with the following results.

Table II

DISTRIBUTION OF DYE

Total volume of solution, 130 cc. Unbleached poplar (soda process), 2.25 g. (bone-dry weight). Time of dyeing, 15 minutes. Temp., 20°.

Dye used G.	Dye in pulp G.	Dye unadsorbed G.	Approximate ratio of dye unadsorbed to dye on fiber
0.0150	0.0128	0.0022	1:6
.0300	.0224	.0076	2:6
.0450	.0291	.0159	3:6

¹⁵ Dreaper, "The Chemistry and Physics of Dyeing," J. and A. Churchill, London, 1906.

¹⁶ Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921.

¹⁷ Pulp obtained through the courtesy of the District of Columbia Paper Mfg. Co.

These results cannot be explained until some method is found of separating the adsorbed and unabsorbed dye on the fiber.

The optical method indicates that there is an actual solution of the dye in the fiber. The next step in explaining the mechanism of dyeing must be to find some method which will separate the dissolved dye from that held on the fiber by adsorption.

Summary

A study of the absorption spectra of light reflected from dyed materials showed that the reflection spectra more nearly explained the variations in color between two dyes than the transmission spectra of the solutions.

Dyeings made on wool, paper and gelatin indicated that the dye was present as a solution in these materials.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY COLLEGE OF SCIENCE OF CALCUTTA]

THE TEMPERATURE OF EXPLOSION FOR ENDOTHERMIC SUBSTANCES. II. TRINITRO-META-CRESOLATES AND THEIR EXPLOSION TEMPERATURES

By Rasik Lal Datta, Loknath Misra and Jogendra Chandra Bardhan Received July 2, 1923

The temperature of explosion has already been studied in the case of a few typical organic compounds, namely, nitro-bodies, picrates, azo compounds, haloid compounds, organic perchlorates, alkaloids, etc.¹ All of these classes of substances are endothermic and hence give explosion temperatures. Previous to our investigations, the explosion temperatures of a very few substances which explode before melting or decomposing were known and for endothermic substances generally such a temperature was never before known to exist. Several of the endothermic substances were, because of their practical use as explosives, known to explode by means of detonators and some of these were shown by Berthellot² to explode when thrown into a vessel previously raised to a high temperature.

The object of these investigations is to show that endothermic substances in general give an explosion temperature, and how the temperature varies according to the endothermic properties and molecular grouping. The reason why such an important constant has previously escaped detection is that substances which either melt or decompose at temperatures below the explosion temperature could not at all attain that temperature in the ordinary course of heating. The temperature is known only for those substances which explode before they are decomposed or volatilized.

¹ Datta and Chatterjee, *J. Chem. Soc.*, 115, 1006 (1919). Previous communication on the subject.

² Berthellot, Compt. rend., 105, 1159 (1887); 129, 926 (1899).

This is clearly evident when we examine how Silberrad and Phillips³ did not obtain the explosion temperatures of trinitrophenol and its ammonium, hydrazine and mercury salts, while they were successful with all the stable metallic salts of trinitrophenol which do not decompose or volatilize before the temperature of explosion is reached. The trinitrophenol is decomposed and the ammonium and hydrazine salts volatilized before the temperature of explosion is attained. This temperature can be determined in air, or in an atmosphere of inert gas such as carbon dioxide and nitrogen or in a vacuum. The method of determination as described in the previous communication on the subject was to drop small quantities of the substances to the bottom of a clean test-tube immersed in a bath of potassium hydrogen sulfate just when the temperature particular to each substance had been attained. The extreme accuracy and reliability of this temperature as an important physical constant for all endothermic substances will be evident from the practical determination of the explosion temperature of acenaphthene-trinitro-m-cresolate. This test was performed at 5°intervals from 350° to 450° without explosion, but at 455° the substance exploded. The bath was cooled, and tests were made at 445° and 450° without explosion, but at 452° explosion occurred. The bath was again cooled and tests made at 448° and 450° without explosion, but at 451° explosion occurred. Once more the bath was cooled and a test made at 450° without explosion, but at 451° explosion again took place. It is thus evident that the temperature of explosion is sharp and quite accurate; the explosion at 451° was marked by a vivid flash of light.

The temperature of explosion should be of great value in determining the purity of endothermic substances which do not give either a melting or a boiling point, since it has been found that the explosion temperature is elevated markedly in the presence of traces of moisture and other impurities. A perfectly pure substance gives the correct explosion temperature, just as it gives correct boiling and melting points.

Furthermore, this constant should be of great practical importance in the manufacture of explosives. It is generally a fact that the lower the temperature of explosion, the easier the substance is exploded and hence the smaller the charge of detonator needed. By determining the explosion temperature of a given explosive, the charges of detonator which would be necessary to explode it satisfactorily may be found at once by comparison with a known explosive having a similar temperature of explosion; no practical tests whatever should be necessary.

Experimental Part

In Table I are listed the names, formulas, properties, analyses, and explosion temperatures of 19 compounds with trinitro-m-cresol. The

³ Silberrad and Phillips, J. Chem. Soc., 93, 475 (1908).

Table I
Preparation and Properties of Trinitro-Meta-Cresolates

					-		An	-Analyses-	THE CO. BY THE SPICE AS NOT A CONTRACT.	-	
			Color						-	,	Expt.
Commission		Cryst.	and	M. p.	Subs.	N	Conditions	ions	Cale	Found t	emp
Compound	Formula	trom	iorm	౪	ග්	Cc.	ಭ	Mm.	%	%	<u>ن</u>
Acenaphthene	CraHio.Tra	alc.	yellow feathers	120	0.0363	4.3	30	758	13.13	13.04	451
Audiene	CisHio.T	bz.	deep yellow needles	109	0.1049	10.2	30	753	10.27	10.64	421
Anylamine	3C3H7N.T	alcbz,	shining yellow	165	0.0556	6.6	23.5	994	20.27	20.32	265
					0.5067	10.1	24	765		20.44	
Benzylamine	C7H9.N.T	H_2O	gold-yellow needles	185	0.1206	17.4	30	760	16.00	16.06	406
Camphylamine	C10H19N.2T	H20	lemon-yellow needles	183	0.0648	8.7	23	992	15.33	15.48	391
Menthylamine	C10H21N.2T	H20	lemon-yellow needles	200		***					
i i	1			decomb.	0.0710	9.5	22.5	266	15.29	15,34	410
riperazine	2C4H10N2.T	alcH ₂ O(1:	alcH.O(1:3) lemon-yellow needles	220 - 225							
				decomb.	0.0691	15.0	31	757.5	23.61	23.79	359
a-Naphthylamine	CloH,N.T	H_2O	dirty yellow needles	165-170							
				decomb.	0.0771	10.0	30	754	14.51	14.32	470
p-Cnloro-anime	C.H.NCI.2T	H20	lemon-yellow needles	170 - 172	0.0696	10.0	56	092	15.98	16.12	449
r-Diomo-anime	CetteNBr.Zl	aq. alc.	lemon-yellow gran.	172.5	0.0593	8.0	30	263	14.89	14.95	441
p-root-annine	CeHeNIZI	dil. alc.	bright yellow needles	152	0.0913	11.4	34	761	13.98	13.70	466
o-Anisidine	CoH4(OCHs)NH2.T	alc.	pale yellow needles	178							
o Discontinuity				decomp.	0.1040	14.3	32	260	15.30	15.18	349
Translatine	Ceta(OC:HE)NH:.T	alc,	bright yellow needles	165	0.1294	17.0	24	764	14.73	14.89	385
Posside mineralina	(CH2)cN4.T	alcbz.		175	0.0336	8.0	36	092	25.58	25.88	325
r seago-cumiquae	CeH2(CH3)3N H3.2T	alc.	velvety yellow needles	183							
7				decomb.	0.0646	0.6	28	260	15.78	15.63	477
Lipaenyiguamdine	(NHC ₆ H ₆) ₂ CNC ₆ H ₆ .T	alc.	brilliant yellow pris-								
Dimothy			matic needles	182	0.0608	8.65	32	760	15.84	15.71	454
α-Naphthol	CioH7N (CH3)2.T	bz.	hard, brilliant plates	154	0.1101	13.8	28	092	13.52	14.06	358
	10118017	an, aic,	orange-yellow silky	1							
B-Nanhthol	£ £		needles	159	0.1288	13.4	30	754	10.83	11.24	472
d 77 a	Cioris. 1	dil. alc.	orange needles	124	0.0685	7.2	30	753	10.83	11.42	452
L = Cert(CH3)(OH)(NO2)3.	(NO2)3.										

compounds with acenaphthene, fluorene, allylamine, benzylamine, p-chloro-aniline and dimethyl- α -naphthylamine were obtained by mixing hot saturated solutions of the constituents and allowing the mixtures to cool slowly.

Camphylamine and α -naphthylamine were dissolved in dil. hydrochloric acid and mixed with hot saturated solutions of trinitro-m-cresolate in water. The menthylamine and piperazine derivatives were prepared from hot aqueous solutions. p-Bromo-aniline was dissolved in water and added hot to an alcoholic solution of the cresol, while alcohol was used for both solutions in the cases of p-iodo-aniline, o-anisidine, o-phenetidine, pseudo-cumidine, triphenyl-guanidine and α -naphthol. The hexamethylenetetramine and β -naphthol compounds were prepared by mixing hot aqueous solutions.

Our thanks are due to the Wolcott Gibbs and C. M. Warren Funds for grants which defrayed part of the expenses of the investigation.

Summary

The temperature of explosion of an endothermic organic explosive substance is a natural constant.

Addition compounds between 19 aromatic amines and phenols and trinitro-m-cresol have been prepared and their explosion temperatures determined.

CALCUTTA, INDIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON CELLULOSE CHEMISTRY

IV. PROPERTIES OF GAMMA-DELTA-DIHYDROXY-CARBONYL DERIVATIVES AND THEIR BEARING ON THE POLYMERIZATION OF POLYSACCHARIDES

By Harold Hibbert and John Arrend Timm^{1,2}
Received July 7, 1923

The suggestion was made by one of us some years ago³ that cellulose was probably derived from an anhydro glucose of the type of Formula I and this was termed the cellulose nucleus.

In a later paper⁴ a comprehensive review was made of the reactions to which any formula for cellulose must conform and opportunity was taken to emphasize the importance of the role played by the hydroxyl groups in the γ,δ positions to the —CHO radical.

- ¹ This paper is constructed from Part II of a dissertation presented by John Arrend Timm in June, 1922, to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.
- ² Communicated to the Cellulose Section, American Chemical Society, Birmingham, Alabama, April, 1922.
 - ³ Hibbert, Chem. Met. Eng., 22, 838 (1920).
 - ⁴ Hibbert, J. Ind. Eng. Chem., 13, 256, 334 (1921).

The question as to whether cellulose is merely a polymerized form of the above nucleus or consists of a closed ring containing (x) anhydro glucose molecules, as shown in Formula II, was left open, no definite information being available at that time as to the magnitude of (x).

That this view was clearly expressed is evident in the current literature. In view of Irvine's recent comments it should be pointed out that no claim has ever been made other than that the cellulose molecule in all probability consists of a large ring of anhydro glucose molecules, each connected to the other through the aldehydic and δ -hydroxyl oxygen linkages, respectively. This view was put forward at a time when no experimental data were available to either confirm or disprove such a theory and it is only through the brilliant series of investigations carried out by Irvine and his collaborators and pupils that the matter is now approaching a settlement, the evidence submitted strongly favoring the constitution of cellulose as represented by Formula III.

It is of interest that their work should confirm the speculations first put forward by one of us⁴ as to the mode of linking of the anhydro glucose units and of the fundamental importance of the γ,δ -hydroxyl groups in the glucose molecule.

If, as previously assumed, the polymerization of anhydro glucose to cellulose is fundamentally related to the behavior of, and dependent on, the loss of water from the δ - and aldehydic hydroxyls, then presumably other γ , δ -dihydroxy-carbonyl derivatives should exhibit the same behavior, and this is now found to be the case.

⁵ Cross and Dorée, "Researches on Cellulose," Longmans, Green and Co., Part IV, 1922.

⁶ Irvine and Hirst, J. Chem. Soc., 123, 527 (1923).

Polymerization of γ , δ -Dihydroxybutyl-methyl Ketone.— γ , δ -Dihydroxybutyl-methyl ketone (CH₂OH—CHOH—CH₂—CH₂—CO—CH₃) was first prepared by Traube and Lehmann⁷ and is a pale yellow, viscous liquid which distils without decomposition at 190° under a pressure of 20 mm. Its mode of synthesis leaves no doubt as to the position of the hydroxyl groups relative to the carbonyl (CO) radical. When this ketone is heated at 120–130° in the presence of a trace of mineral acid (concd. sulfuric acid) for a few minutes, water is evolved and the liquid becomes more and more viscous, the dark-colored, very viscous product solidifying to a hard, compact resin at room temperature. This reaction also proceeds in the presence of this catalyst at room temperature, though much more slowly.

A determination of the amount of water evolved, and an analysis of the resin, show that the latter is derived from the dihydroxy ketone by the loss of one molecule of water from each molecule of the ketone. Assuming that the ketone possesses the butylene oxide structure⁸ the changes taking place may presumably be represented as follows:

⁷ Traube and Lehmann, Ber., 34, 1971 (1901).

⁸ The constitution of dihydroxybutyl-methyl ketone has not yet been definitely established. A decision as to whether it contains (a) a butylene or (b) an amylene oxide ring can presumably be reached by employing the technic developed by Irvine. Thus by converting it into the methyl ketoside, followed by methylation, hydrolysis, and oxidation (a) should yield a 1:4 diketone, while (b) should give a ketonic acid. This work is in progress as well as the synthesis of the corresponding aldehyde (CH₂-OHCHOHCH₂CH₂CHO), an examination of whose properties is expected to yield further valuable information. The senior author courteously requests that he may be left undisturbed in the prosecution of this work for a limited period.

the reaction thus representing an *intramolecular cyclic acetal condensation*. Such a reaction would seem to be of considerable importance when considered in the light of its bearing on the formation of inulin from fructose, starch and cellulose from glucose, etc.

There is one other explanation as to the course of the above reaction, namely, the primary splitting off of water to give an ethylene oxide ring,

followed by polymerization to the resinous product,

$$\begin{array}{c} \text{CH}_2\text{-CH}\text{-CH}_2\text{-CH}_2\text{-CO}\text{-CH}_3 \\ \text{CH}_2\text{-CH}\text{-CH}_2\text{-CH}_2\text{-CO}\text{-CH}_3 \\ \text{O} \end{array} \\ \begin{array}{c} \text{CH}_2\text{-CH}\text{-CH}_2\text{-CH}_2\text{-CO}\text{-CH}_3 \\ \text{O} \\ \text{O} \\ \text{O} \end{array} \\ \begin{bmatrix} \text{CH}_2\text{-CH}\text{-CH}_2\text{-CH}_2\text{-CO}\text{-CH}_3 \\ \text{O} \\ \text{O} \\ \end{bmatrix}_X \end{array}$$

That this does not occur was proved by the direct synthesis of B from allyl acetone by treating the latter with hypochlorous acid to give the chlorohydrin and then removing hydrochloric acid with formation of the oxide, which was first prepared in this manner by Kablukow, (B). On warming with a drop of concd. sulfuric acid, this oxide shows no tendency to polymerize, prolonged heating resulting only in charring.

The results thus obtained provide valuable experimental support for previous speculations relative to the role played by hydroxyl groups in the γ and δ positions to the carbonyl radical and of their function in the polymerization processes leading to the formation of polysaccharides. The importance of these groups is being further emphasized by Irvine and his school in connection with the properties of the γ sugars as related to vital problems such as the abnormal metabolic changes taking place in cases of diabetes.

Experimental Part

Preparation of γ , δ -Dihydroxybutyl-methyl Ketone.—The ketone was prepared by the method of Traube and Lehmann⁷ by heating together epichlorohydrin and the sodium salt of ethyl aceto-acetate. The sodium salt of 1-chloro-2-hydroxypropyl-ethyl aceto-acetate, first formed, decomposes, yielding sodium ethylate and α -acetyl- δ -chloro- γ -valerolactone. The lactone, on boiling with a dilute solution of potassium carbonate, yields the γ , δ -dihydroxybutyl-methyl ketone.

Method.—Twelve g. of sodium was dissolved in absolute alcohol and 70 g. of aceto-acetic ester added. The mixture was cooled to 0° and 50 g. of epichlorohydrin, dissolved in 50 cc. of absolute alcohol, was added drop by drop in the course of about two hours. The alcohol was then evaporated under reduced pressure and the residue treated with 500 cc. of 5% sulfuric acid. The oily layer which separated was dried over sodium

⁹ Kablukow, J. Russ. Phys.-chem. Soc., 1, 502 (1887); Ber. Ref., 21, 55 (1888).

sulfate and, on fractionation under reduced pressure, yielded 40 g. of the lactone, b. p., 163° (12 mm.), which corresponds to that obtained by Traube and Lehmann.

Forty g. of α -acetyl- δ -chloro- γ -valerolactone was boiled with 0.5 mole of potassium carbonate in the form of a 5% aqueous solution for 5 hours. The oil gradually dissolved with evolution of carbon dioxide. After removal of the water under reduced pressure at about 25°, the remaining oil was dissolved in absolute alcohol, the solution filtered from the potassium chloride, dried over sodium sulfate, and the alcohol removed by distillation. The remaining oil, on fractionation, yielded 8 g. of γ , δ -dihydroxybutylmethyl ketone, b. p., 158–160° (7–8 mm.) [b. p., 189–191° (20 mm.)], which is in agreement with that found by Traube and Lehmann).

Conversion of Dihydroxybutyl-methyl Ketone into its Anhydro Derivative.—Prepared as outlined above, the dihydroxy ketone is a pale yellow, viscous liquid which distils under diminished pressure without decomposition if all traces of acid are carefully removed. It also undergoes no apparent change after standing at room temperature for months. However, when it is heated under atmospheric pressure in the presence of traces of concd. sulfuric acid at about 125°, dehydration followed by resinification takes place.

Fifty g. of dihydroxybutyl-methyl ketone was mixed with 0.05 g. of concd. sulfuric acid and the mixture heated to 150° . The liquid rapidly became very viscous, water was evolved and after 2–3 minutes it solidified on cooling to a hard resin. This was pulverized, dried for two hours at 100° , and analyzed.

Analyses. Calc. for $C_6H_{10}O_2$: C, 63.11; H, 8.84. Found: C, 62.86, 62.91; H, 9.01, 9.11.

The analysis indicates that the product has been formed by the loss of one mol. of water from each molecule of the dihydroxybutyl-methyl ketone ($C_6H_{12}O_3 = C_6H_{10}O_2 + H_2O$), a conclusion confirmed by the direct weighing of the water evolved during the resinification process.

This was carried out by placing a known weight of the ketone in a small glass-stoppered tube (about 8 cc. in capacity, 10 cm. long and 1 cm. in diameter). This was fitted with a narrow inlet and outlet tube, the latter being connected to a weighed U-tube containing concd. sulfuric acid; 0.01 g. of concd. sulfuric acid was then introduced, the stopper inserted and the mixture heated to 120–130° in a current of dry air for about 6 hours to constant weight.

Analysis. Subs., 0.7956: H_2O obt. 0.1177; actual loss in weight of ketone product, 0.1337 g., or 16.8%. Calc. for 1 molecule loss of water: H_2O , 13.64%. Found: 14.79.

There is apparently some slight secondary decomposition brought about by the long continued heating under these conditions.

Preparation of γ -Ketobutyl-ethylene Oxide. CH_2 -CH- CH_2 - CH_2 -

CO—CH₃.—This was made according to Kablukow's method⁹ from allyl acetone.

Allyl Acetone.—Allyl acetone was obtained by condensing allyl bromide with the sodium salt of aceto-acetic ester¹⁰ and saponifying the allyl-ethyl aceto-acetate, thus formed, with dil. potassium carbonate solution.

¹⁰ Wolff, Ann., 201, 46 (1880).

Mehrling's¹¹ method of hydrolysis with barium hydroxide was found unsatisfactory. The following modified procedure gave satisfactory results, but the yield was never high because of the formation of by-products.

One hundred g. of allyl-ethyl aceto-acetate was boiled for 20 hours with 300 cc. of a 5% potassium carbonate solution, the mixture being thoroughly agitated throughout. The product was then steam distilled, the upper allyl acetone layer in the distillate separated and the aqueous layer extracted with ether. The ether extract was dried over sodium sulfate and finally distilled. Yields of about 35% allyl acetone (b. p., $129-134^\circ$) were usually obtained.

Allyl Acetone Chlorohydrin.—The hypochlorous acid solution was prepared according to the method of Bamberger and Lodter. 12

Two hundred g. of bleaching powder was suspended in water and allowed to stand for 24 hours in the dark at 40° , 115 g. of sodium carbonate was then introduced and the suspension thoroughly shaken. It was then filtered by suction and 160 g. of pulverized boric acid added to the filtrate.

To 100 cc. of this solution, 10 g. of allyl acetone was slowly added in the course of one hour, the mixture being agitated and the temperature kept below 0°. The solution was also protected from direct light. After standing for 12 hours another 200 cc. of the hypochlorous acid solution was added and the solution allowed to stand under the same conditions for an equal length of time. It was then extracted with ether, dried over sodium sulfate, the ether removed, and the remaining oil fractionated under reduced pressure; yield, 8 g.; b. p., 113° (20 mm.), which corresponds to that obtained by Kablukow.

Conversion of the Chlorohydrin into the Oxide.—Eight g. of allyl acetone chlorohydrin was heated with 200 cc. of 5% potassium carbonate solution on a water-bath for 16 hours and then at the boiling point on a sand-bath for 10 hours. The solution was cooled, extracted with ether, dried, and the ether removed by distillation. No residue remained. The mother liquor was then carefully neutralized with hydrochloric acid and the water evaporated on a steam-bath. A viscous oil remained which was dissolved in alcohol, filtered, and dried over sodium sulfate; the alcohol was then removed, and the residue distilled under diminished pressure. The oxide was obtained as a colorless, mobile liquid; b. p., 169° (81 mm.); yield, about 2 g.; the boiling point recorded by Kablukow was 162–167° at 80 mm. When a portion of the oxide was heated with a drop of concd. sulfuric acid no indication of any polymerization could be observed, but prolonged heating resulted in some charring.

The authors desire to acknowledge gratefully the kind assistance rendered them for the purchase of supplies in the form of a grant from the Warren Fund of the American Academy of Arts and Sciences.

Summary

- 1. Attention is drawn to the important role played by the γ and δ -hydroxyl groups in the conversion of carbohydrates to polysaccharides.
- 2. It is found that the simplest γ, δ -dihydroxy-ketone, namely, γ, δ -dihydroxybutyl-methyl ketone, readily undergoes dehydration and polymerization in the presence of a trace of mineral acid. The change corre-

¹¹ Mehrling, Ann., 264, 323 (1891).

¹² Bamberger and Lodter, Ann., 288, 81 (1895).

sponds to a loss of one molecule of water from each molecule of the dihydroxy ketone.

3. The polymerization taking place is probably closely related to that occurring in the formation of inulin from fructose.

New Haven, Connecticut

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

TRIHYDROXY-METHYL-ANTHRAQUINONES. 1

By G. D. Graves¹ with Roger Adams Received July 23, 1923

Hydroxy-methyl-anthraquinones and their methyl ethers occur widely, either in the free state or as glucosides, in the leaves, bark and roots of various plants, forming natural drugs and coloring matters. Six natural trihydroxy-methyl-anthraquinones have been reported in the literature, the most important being emodin, found in Cascara sagrada, Frangula, rhubarb and other plants. The probable structures which have been suggested for a few of these anthraquinones contain two hydroxyl groups in one ring, with the methyl and remaining hydroxyl in the other. A study of a practical method of synthesis of this type of substituted anthraquinones has been undertaken with the ultimate object of synthesizing the natural products.

In general, the best method available for the preparation of substituted anthraquinones with definite structures is the condensation of phthalic anhydride or its derivatives with benzene derivatives to form substituted benzoyl-benzoic acids; these can then be dehydrated to give anthraquinones. To prepare the desired trihydroxy-methyl-anthraquinones it was proposed to condense dimethoxy-phthalic anhydrides with the cresols, to dehydrate the resulting benzoyl-benzoic acids, and to demethylate the anthraquinones.

But few condensations involving methoxy-phthalic anhydrides have been reported. Bistrazycki² condensed 3,4-dimethoxy-phthalic anhydride (hemipinic anhydride) with anisole by means of aluminum chloride, using benzene as a solvent. The same anhydride was condensed by Weizmann³ with veratrol, pyrogallol-trimethyl ether and o-xylene, using aluminum chloride with carbon disulfide as a solvent. Simonsen condensed this anhydride with o-cresol by means of aluminum chloride in acetylene tetrachloride.⁴ With the exception of the condensation product of hemipinic anhydride with anisole, the exact structure of the resulting products

¹ This communication is an abstract of a thesis submitted by G. D. Graves, DuPont Fellow for 1922–1923, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Bistrazycki, Ber., 31, 2796 (1898).

³ Weizmann, J. Chem. Soc., (a) 91, 1626 (1907); (b) 93, 435 (1908); (c) 105, 2748 (1914).

⁴ Simonsen, ibid., 119, 1339 (1921).

was not determined. In the particular case just mentioned it was shown without question that the carboxyl group adjacent to the methoxy group entered into reaction and that it condensed *para* to the methoxy group of the anisol.

Weizmann³ condensed 4-methoxy-phthalic anhydride with o-xylene and p-cresol methyl ether by means of aluminum chloride in carbon disulfide, and with the free cresols by means of boric acid; Dimroth and Fick⁵ condensed 3-methyl-5-methoxy-phthalic anhydride with hydroxy-hydroquinone triacetate by means of boric acid. The exact course of these condensations was also left undetermined. Moreover, in almost all of the condensations just reviewed the results were quite unsatisfactory.

A systematic study of the synthesis of such trihydroxy-methyl-anthraquinones of definite structures from methoxy-phthalic anhydrides must involve a thorough knowledge of four points: the best method for the initial condensation to form the benzoyl-benzoic acid derivatives; the best method for dehydrating the benzoyl-benzoic acids to form anthraquinones; the position in the cresol ring (whether *ortho* or *para* to the hydroxyl) taken by the entering benzoyl radical; the determination of which of the two carboxyl groups in an unsymmetrical phthalic anhydride reacts first with the cresol.

This research has involved a study of the condensation of 3,6-dimethoxy-phthalic anhydride with o-, m- and p-cresols. The structure of the benzoyl-benzoic acids formed has been determined and a study of their conversion into anthraquinones has been made. Preliminary work upon the condensation of 3,5-dimethoxy-phthalic anhydrides and cresols has been carried out.

On account of its ease of preparation, 3,6-dimethoxy-phthalic anhydride was chosen as a convenient methoxy-phthalic anhydride to employ in determining a satisfactory method of condensation with the various cresols. It has the further advantage of being symmetrical in structure, thereby eliminating a problem which is involved with unsymmetrical phthalic anhydrides, namely, the determination of which carboxyl reacts first with the cresol.

Many of the commoner methods of effecting condensation of phthalic anhydrides with various types of cresols gave unsatisfactory results with the 3,6-dimethoxy derivative. Thus, boric acid gave very poor yields, and the method of Ullmann and Schmidt,⁶ using aluminum chloride and acetylene tetrachloride, caused the decomposition of the anhydride. Satisfactory results were obtained by using excess of cresol as a solvent⁷ and a rather

- ⁵ Dimroth and Fick, Ann., 411, 315 (1915).
- ⁶ Ullmann and Schmidt, Ber., 52, 2098 (1919).

⁷ During the preparation of this manuscript an article has appeared by Widmer [Helvetica Chim. Acta, 6, 421 (1923)] in which a similar method of condensation of certain phthalic anhydrides with phenols was employed with success.

large proportion of aluminum chloride. Under these conditions consistent results were obtained. 3,6-Dimethoxy-phthalic anhydride formed benzoyl-benzoic acid derivatives when condensed with the cresols and at the same time yielded diphenyl-phthalide derivatives as by-products.

Acids I, II and III were obtained from o-, m- and p-cresols in 22%, 50% and 16% yields, respectively. In each reaction, a certain amount of diphenyl-phthalide derivative formed, a phthalein from both o- and m-cresol (IV and V) and a fluoran from p-cresol (VI).

Although the yields of benzoyl-benzoic acids appear small, the ease with which they could be separated and purified rendered the processes practicable.

For the dehydration of the benzoyl-benzoic acids to form anthraquinones, concd. or fuming sulfuric acid, sometimes with boric acid, has almost always been used. These reagents have proved satisfactory for many of the methoxy compounds studied. Concd. sulfuric acid with a trace of boric acid readily converted the condensation products from o- and p-cresol (I and III) into the corresponding anthraquinones (VII and IX) in 30% and 88% yields, respectively. In the case of the m-cresol, however, ordinary concd. sulfuric acid gave no results and only by the use of 7% fuming acid was it possible to obtain a 6% yield of the corresponding anthraquinone (VIII).

A similar difficulty in the formation of anthraquinones from those benzoylbenzoic acids which contain an *ortho* or *para* directing group *meta* to the position in which condensation must take place was observed by Weizmann.⁸ This difficulty was particularly pronounced in the case of phenol derivatives probably on account of the ease with which sulfonation took place. Widmer⁹ reports the formation of an anthraquinone from a *m*-cresol-benzoyl-benzoic acid by means of fuming sulfuric acid, but does not state his yield.

Under the conditions used for forming the anthraquinones from the benzoyl-benzoic acids, there was only a slight splitting of the methyl ethers during the condensation. In general, if temperatures higher than 100° were employed, the splitting of the ethers became appreciable and sulfonation took place to a greater extent. For the conversion of the methylated anthraquinones to the corresponding hydroxy anthraquinones (X, XI and XII), aluminum chloride in benzene may be used. It was found, however, that better results could be obtained by heating with constant-boiling hydrobromic acid in acetic acid solution.

The structure of the benzoyl-benzoic acids was determined by a comparison of the compounds obtained from the free cresols and the cresol ethers. The assumption was made that the entering group would be either ortho or para to the hydroxyl, since no condensations of this type have ever been known to enter the meta position. Nourrisson¹⁰ and Weizmann³ have already shown in a number of instances that phthalic anhydride and certain derivatives condensed with phenol ethers in the para position to the methoxyl group. Other investigators 11 have found that with free phenols the entering group goes ortho to the hydroxyl. By analogy, it seems reasonably certain that the structures of the compounds obtained in this investigation are correct as given. To confirm this conclusion the benzoyl-benzoic acids from 3,6-dimethoxy-phthalic anhydride and o- and m-cresols were methylated to give the trimethyl ethers. These products differed from the trimethyl ethers¹² obtained by the condensation of phthalic anhydride and cresol ethers, showing definitely that a different position was taken in each of the condensations. The condensation product from p-cresol, when methylated, gave the same substance as that obtained by the condensation product from p-cresol methyl ether. This would be expected because the para positions to the hydroxyl and methoxyl

⁸ Weizmann, Ref. 3a; J. Chem. Soc., 95, 279 (1909).

⁹ Widmer, Helvetica Chim. Acta, 5, 1 (1922).

¹⁰ Nourrisson, Ber., 19, 2103 (1886).

¹¹ Bentley, Gardner and Weizmann, J. Chem. Soc., 91, 1626 (1907). Ref. 6.

¹² See the following paper by Gardner and Adams.

groups in p-cresol and p-cresol methyl ether, respectively, are filled, and consequently the *ortho* position will be taken in both condensations.

Further evidence concerning the character of the condensation products came from a study of the decomposition of the phthaleins. It has already been mentioned that when the cresols were condensed with 3,6-dimethoxy-phthalic anhydride, diphenyl-phthalide by-products were obtained. The phthaleins from the o- and m-cresol condensations resemble phenol- and cresolphthalein very closely and the products, therefore, unquestionably have the structure represented by Formulas IV and V. In the case of the p-cresol, phthalein condensation must take place in the ortho position to the hydroxyl, thus allowing the formation of a fluoran by dehydration (VI). If, for any reason, the phthaleins had formed in the ortho position to the hydroxyl in either the o- or m-cresol condensations, it is extremely probable that fluorans would also have formed spontaneously.

The phthalein (IV) from the o-cresol condensation, when heated with 3,6-dimethoxy-phthalic anhydride in sulfuric acid, was converted according to the general method of Baeyer¹³ into an anthraquinone derivative. This anthraquinone (XIII), however, should be different from that (X) obtained by the dehydration of the benzoyl-benzoic acid from 3,6-dimethoxy-phthalic anhydride and the free o-cresol and then demethylation of the anthraquinone produced; but it should be identical with the trihydroxy-methyl-anthraquinone¹⁴ formed by the condensation of 3,6-dimethoxy-phthalic anhydride with o-cresol methyl ether, followed by condensation to the anthraquinone and demethylation.

The experimental results were exactly those expected, the substances obtained checking up in every particular. The fact that the anthraquinone formed according to the above equation has the structure XIII and not the possible isomeric structure XIV is proved in the following paper.¹⁴

The condensation of 3.5-dimethoxy-phthalic anhydride and m-cresol (XV) was carried out. It went smoothly as might be expected from the

¹³ Baeyer and Freude, Ann., 202, 137, 165 (1880).

¹⁴ Gardner and Adams, This Journal, 45, 2455 (1923).

results with the 3,6-dimethoxy-phthalic anhydride and *m*-cresol. It seems probable that the condensation took place through the carboxyl adjacent to the methoxyl group judging by analogy to hemipinic anhydride condensations, but this has not yet been proved.

In order to show that condensation with the 3,5-dimethoxy-phthalic anhydride followed the same course as the condensation with 3,6-dimethoxy-phthalic anhydride, that is ortho to the hydroxyl and para to the methoxyl. 3,5-dimethoxy-phthalic anhydride was condensed with m-cresol methyl ether. A different trimethoxy-benzoyl-benzoic acid (XVI) was obtained from that formed by the methylation of the condensation product XV obtained from the free m-cresol. Proof of the structure of the condensation products was indicated by condensing 3.5dimethoxy-phthalic anhydride with o-nitro-m-cresol, obtaining undoubtedly the acid XVIII because there would be practically no tendency for the benzovl group to enter between the hydroxyl and methyl groups, and the other ortho position to the hydroxyl group is filled. This was not identical with the nitration product from the acid XV which, doubtless, then has the structure XIX. Had condensation with m-cresol gone para to the hydroxyl group to form the acid XVII, nitration would undoubtedly have given the acid XVIII.

The condensation product of 3,5-dimethoxy-phthalic anhydride and *m*-cresol (XV) should by dehydration and demethylation give emodin, provided the structure¹⁵ XX which has been assigned to it after a careful study of its reactions is correct. When the ring closure was attempted, however, even poorer yields were obtained than with the *m*-cresol condensation product from 3,6-dimethoxy-phthalic anhydride. The product was methylated to form the trimethyl ether and this was compared with the trimethyl ether from emodin. Natural emodine and the synthesized dimethyl ether dissolved in alkali with the development of & red color. The synthetic trimethyl ether and that from cascara emodin dissolved

¹⁵ Arch. Pharm., 250, 301 (1912). Hesse [Ann., 309, 73 (1899)] had previously suggested that emodin might have the structure of the anthraquinone (XII) prepared as described above.

in concd. sulfuric acid with the same red color. The absorption spectra of the trimethyl ethers showed close similarity in their curves.

Although only a very small amount of the anthraquinone was obtained, all indications pointed toward its being an emodine derivative. Further work is now under way modifying this latter condensation in such a manner that the preparation of emodine in satisfactory yields should be possible and the constitution of this substance thus be proved without question.

Absorption Spectra of the Anthraquinones and Phthaleins 16

The absorption spectra and color reactions of anthraquinones are accepted as furnishing very reliable evidence concerning the orientation of hydroxyl groups. Absorption-spectra curves for all of the anthraquinones prepared were obtained by the method recommended by the United States Bureau of Standards. As abscissas are plotted wave lengths in $(m\mu)$ and as ordinates, $-\log_{10}$ transmission, which is defined as the ratio of the intensities of the light leaving to the light entering the absorbing layer, that is, $bck = -\log T$, where b is the concentration and c the thickness. The concentration of the solutions used was not determined so that the values of the ordinates have no significance; this does not interfere with the determination of the wave length of the absorption bands.

The absorption of slightly acid and alkaline alcoholic solutions was determined, the alcohol being used to accentuate the peaks of the curves. The solutions for determination were prepared by adding to the alcoholic solutions of the anthraquinones just enough alcoholic alkali to change the color, or a drop of alcoholic hydrochloric acid. All of the curves of the anthraquinones having the quinizarin grouping (two α -hydroxyl groups in the same ring) have the same general form, the acid absorption band being nearer the blue than the alkaline band (Fig. 1). The maxima of the dimethoxy-hydroxymethyl-anthraquinones were 15-20m μ nearer the blue than those of the corresponding trihydroxy compounds (Fig. 2). The bands shifted toward the red in the 1,5,8-trihydroxy-anthraquinones as the methyl group moved from Position 2 to 4 to 3.

The phthaleins (IV and V) are very similar to phenolphthalein, giving blue-red colors with alkali. They are indicators, changing color at $P_{\rm H}$ values of 9.1 and 9.8, respectively, phenolphthalein and o-cresolphthalein changing at Sörensen values of 8.3 and 8.2, respectively.

The alkaline absorption curves were very similar, Phthaleins V and VI showing maxima at $\lambda 580$ and $\lambda 585$, respectively, while the maxima of

 $^{^{16}}$ The authors are indebted to Mr. Wallace R. Brode for his assistance in determining the absorption spectra.

¹⁷ Bull., 440, 128 (1922).

¹⁸ A Keuffel and Esser spectrophotometer was used.

¹⁹ Meek, J. Chem. Soc., 109, 554 (1916).

phenolphthalein and o-cresolphthalein are at $\lambda555$ and $\lambda572$, respectively. The curves are of the same general type as that obtained from phenolphthalein.

Experimental Part

Preparation of 3,6-Dimethoxy-phthalic Anhydride. 2,3-Dicyanohydroquinone, $C_6H_2(OH)_2(CN)_2$.—This substance was prepared by the method of Thiele and Meisen-

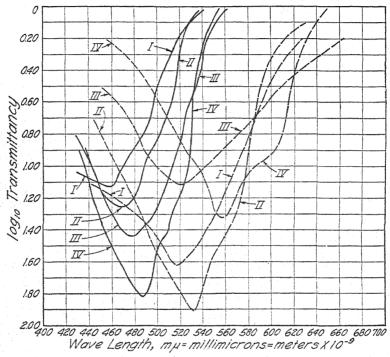


Fig. 1.—The solid lines represent the curves obtained from the alcoholic hydrochloric acid solutions, and the dotted lines the curves from the alcoholic sodium hydroxide solutions of the various anthraquinones. Readings were taken every $0.1 \log T$.

I. 1,5,8-Trihydroxy-2-methyl-anthraquinone. II. 2,5,8-Trihydroxy-1-methyl-anthraquinone. III. 1,5,8-Trihydroxy-4-methyl-anthraquinone. IV. 1,5,8-Trihydroxy-3-methyl-anthraquinone.

heimer²⁰ by the action of hydrocyanic acid on quinone in alcoholic solution. No product could be obtained by the method of Helferich.

2,3-Dicyanohydroquinone Dimethyl Ether, $C_6H_2(OCH_3)_2(CN)_2$.—This substance has previously been made by the action of methyl iodide on 1,3-dicyanohydroquinone. A solution of 60 g of potassium hydroxide in 300 cc. of water was made in a 5-liter flask. Before this had cooled, 60 g of dicyanohydroquinone was dissolved in it, and 240 g of dimethylsulfate added. The flask was shaken vigorously until the reaction mixture

²⁰ Thiele and Meisenheimer, Ber., 33, 675 (1900); Frdl., VI, 113 Ger. pat. 117,005. Helferich, Ber., 54, 155 (1921).

²¹ Thiele and Günther, Ann., 349, 59 (1906).

third 300cc. portion of alkali was added, the flask shaken, and set aside to cool. After several hours the product was filtered off and washed thoroughly with cold water. The yield was 64 g. (85%) of a product which after a crystallization from acetic acid melted at 275°.

3,6-Dimethoxy-phthalic Anhydride, C₆H₂(OCH₃)₂(CO)₂O.—Thiele and Günther²³ hydrolyzed dicyanohydroquinone dimethyl ether to the corresponding phthalimide by

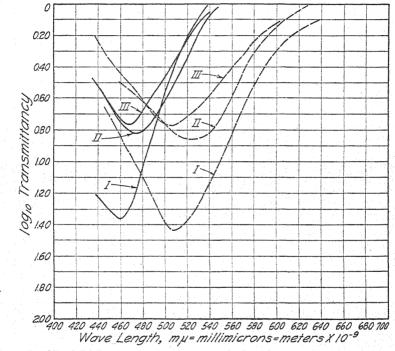


Fig. 2.—The solid lines represent the curves obtained from the alcoholic hydrochloric acid solutions, and the dotted lines the curves from the alcoholic sodium hydroxide solutions of the various anthraquinones. Readings were taken every $0.1 \log T$.

I. 1-Hydroxy-2-methyl-5,8-dimethoxy-anthraquinone. II. 1-Hydroxy-3-methyl-5,8-dimethoxy-anthraquinone. III. 1-Hydroxy-4-methyl-5,8-dimethoxy-anthraquinone.

means of sulfuric acid. The phthalimide was converted to the anhydride by alcohol and hydrochloric acid.

The same results could not be obtained by following the directions given. It has been found possible to convert the nitrile directly to the anhydride by means of sulfuric acid.

²² All melting points given in this paper are corrected unless otherwise stated.

²² Ref. 21. Zincke and Schmidt [Ann., 286, 37 (1895)] also obtained this anhydride by oxidation of 1,4,5,6-tetramethoxy-naphthalene with potassium permanganate.

A mixture of 60 g. of crude dicyanohydroquinone dimethyl ether, 300 cc. of concd. sulfuric acid, and 15 cc. of water was heated on the steam-bath for 1.5 hours. At the end of this time the solution was poured into 500 cc. of water and boiled for two hours. After the mixture had cooled the dimethoxy-phthalic anhydride was filtered off. The yield was 45 g. (64%) when the 2,3-dicyanohydroquinone dimethyl ether was of reasonably good grade. The product, after purification from benzene, melted at 259–261°. Sometimes the total amount did not precipitate at once. It was often necessary to evaporate the filtrate in an open dish overnight on the steam-cone in order to complete the hydrolysis of the nitrile. On the addition of water, the remainder of the anhydride was precipitated.

Condensation of 3,6-Dimethoxy-phthalic Anhydride with the Cresols

p-Cresol Derivatives. 3,6-Dimethoxy-2-(2-hydroxy-5-methylbenzoyl)benzoic Acid (III).—A mixture of 10 g. of 3,6-dimethoxy-phthalic anhydride, 10 g. of aluminum chloride, and 30 cc. of p-cresol was stirred mechanically and heated slowly up to 70° (oil-bath temperature) during the course of 4 hours, then held at that temperature for 9 hours. Water was cautiously added to decompose the excess of aluminum chloride, then 10 cc. of hydrochloric acid, and the excess of cresol was distilled with steam. The liquid remaining in the flask was decanted from the gummy residue which was dissolved in 10% sodium hydroxide solution. The alkaline solution was red, due to phthalein byproducts. It was saturated with carbon dioxide to precipitate the phthalein (2 g.), which was filtered off. The filtrate was acidified with hydrochloric acid to precipitate the benzoylbenzoic acid; yield, 2.5 g. (16%). The product was purified from methyl alcohol, forming white plates; m. p., 218°.

Analyses. Subs., 0.1330; CO₂, 0.3146; H₂O, 0.0620. Cale. for $C_{17}H_{16}O_6$: C, 64.59; H, 5.06. Found: C, 64.51; H, 5.17.

Subs., 0.2243: required, 0.712 cc. of N NaOH. Calc.: neutr. equiv., 316. Found: 315.

2,7-Dimethyl-12,15-dimethoxyfluoran²⁴ (VI).—The phthalein by-product was dissolved in glacial acetic acid. The solution was treated with bone black and allowed to stand in the open for a week or more in order to avoid the separation of amorphous material by rapid precipitation and to allow crystals to form slowly. This material was recrystallized from glacial acetic acid, from dil. acetic acid, and from an acetone-ether mixture, to constant melting point. It was found to be insoluble in alkali, the acetic acid apparently having dehydrated the *ortho*-phthalein to a fluoran. The product formed white crystals that melted at 290°.

Analyses. Subs., 0.0791, 0.1029: CO_2 , 0.2128, 0.2771; H_2O , 0.0378, 0.0493. Calc. for $C_{24}H_{20}O_5$: C, 74.22; H, 5.16. Found: C, 73.37, 73.43; H, 5.30, 5.32.

The material analyzed had not undergone the final purification with acetone and ether and apparently held acetic acid, so that the analyses were not as accurate as might be expected.

About 4 g. of uncondensed dimethoxy-phthalic anhydride was recovered by adding $^{1}/_{3}$ the volume of sulfuric acid to the liquors remaining over the gummy condensation product after steam distillation, and boiling the solution until the anhydride separated. Thus, from the 6 g. of anhydride that reacted, 4.5 g. of mixed product was isolated.

3,6-Dimethoxy-2-(2-methoxy-5-methylbenzoyl)benzoic Acid.—This substance was prepared in quantitative yields by refluxing 1 g. of the 3,6-dimethoxy-2-(2-hydroxy-5-methylbenzoyl)benzoic acid (III), 4 g. of potassium hydroxide, 5 g. of dimethyl sulfate and 75 cc. of water for an hour, filtering, and precipitating the trimethoxy compound with hydrochloric acid. It was recrystallized from dil. methyl alcohol, forming white

²⁴ The nomenclature used is that recommended by Chemical Abstracts.

needles that melted at 203° . It proved to be identical with the compound made from 3,6-dimethoxy-phthalic anhydride and p-cresol methyl ether and described in the following paper by Gardner and Adams.

1-Hydroxy-4-methyl-5,8-dimethoxy-anthraquinone (IX).—Two g. of the 3,6-dimethoxy-2-(2-hydroxy-5-methylbenzoyl)benzoic acid (III), a pinch of boric acid, and 40 cc. of concd. sulfuric acid were heated on the steam-bath for one hour. The color changed from green to bluish red. The solution was poured over ice to precipitate the anthraquinone. It was purified by dissolving in alkali and reprecipitating with carbon dioxide; yield, 1.5 g. (88% of the calculated amount). The material was purified from acetone, forming red needles; m. p., 224°. It gave a red solution in alkali and a blue to blue-red color in concd. sulfuric acid, depending on the concentration.

Analyses. Subs., 0.0620: CO_2 , 0.1566; H_2O , 0.0247. Calc. for $C_{17}H_{14}O_5$: C, 68.46; H, 4.70. Found: C, 68.89; H, 4.47.

1,5,8-Trihydroxy-4-methyl-anthraquinone (XII).—1-Hydroxy-4-methyl-5,8-dimethoxy-anthraquinone (IX) was refluxed with equal parts of constant-boiling hydrobromic acid and glacial acetic acid for 6 hours. The anthraquinone was precipitated by pouring the solution into water and purified by recrystallization from glacial acetic acid. It dissolved in alkali with the development of a blue-red color. In concd. sulfuric acid it showed a blue color in dilute solutions, and a blue-red color in greater concentrations.

Analyses. Subs., 0.0734: CO₂, 0.1784; H_2O , 0.0250. Calc. for $C_{15}H_{10}O_5$: C, 66.66; H, 3.70. Found: C, 66.29; H, 3.78.

o-Cresol Derivatives. 3,6-Dimethoxy-2-(2-hydroxy-3-methylbenzoyl)benzoic Acid (I).—A mixture of 15 g. of 3,6-dimethoxy-phthalic anhydride, 24 g. of aluminum chloride and 60 cc. of o-cresol, stirred mechanically, was heated in an oil-bath at 75 $^{\circ}$ for 19 hours. The products were worked up as in the p-cresol condensation: yield, 5 g. of benzoyl-benzoic acid (22%) and 18 g. of crude phthalein by-product. The benzoyl-benzoic acid was purified from methyl alcohol, forming white needles; m. p., 194°.

Analyses. Subs., 0.0748: CO_2 , 0.1958; H_2O , 0.0352. Calc. for $C_{24}H_{22}O_6$: C, 70.33; H, 5.17. Found: C, 71.02; H, 5.22.

o-Cresol-3,6-dimethoxy-phthalein (2,2-Bis(4-hydroxy-5-methylphenyl)3,6-dimethoxyphthalide) (IV).—This substance was purified in the same way as was 2,7-dimethyl-12,15-dimethoxy-fluoran (VI). It was treated, however, with hot alkali after recrystal-lization from acetic acid in order to saponify any acetyl derivative which might have formed. The product forms white needles; m. p., 258°. The substance is an indicator, changing from colorless to red at $P_{\rm H}$ 9.1. The alkaline absorption spectrum showed a peak at $\lambda 580 {\rm m}\mu$.

Analyses. Subs., 0.0748: CO₂, 0.1948; H₂O₃, 0.0352. Calc. for $C_{24}H_{22}O_6$: C, 70.93; H, 5.17. Found: C, 71.02; H, 5.22.

3,6-Dimethoxy-2-(2-methoxy-3-methylbenzoyl)benzoic Acid.—This was prepared by methylation of 3,6-dimethoxy-2-(2-hydroxy-3-methylbenzoyl)benzoic acid (I) exactly as described under the preparation of 3,6-dimethoxy-2-(2-methoxy-5-methylbenzoyl)benzoic acid. It was purified from methyl alcohol, forming white needles; m. p., 178°. It was not identical with the benzoyl-benzoic acid obtained by condensing 3,6-dimethoxy-phthalic anhydride with o-cresol methyl ether, which has the constitution 3,6-dimethoxy-2-(4-methoxy-5-methylbenzoyl)benzoic acid.

Analyses. Subs., 0.1438: CO₂, 0.3430; H₂O, 0.0700. Calc. for $C_{18}H_{18}O_6$: C, 65.45; H, 5.45. Found: C, 65.12; H, 5.40.

Subs., 0.4642: required, 0.139 cc. of N NaOH. Calc.: neutr. equiv., 330. Found: 333.

o-Cresol-3,8-dimethoxy-phthalein-dimethyl Ether, (2,2-Bis(4-methoxy-5-methyl-phenyl)3,6-dimethoxyphthalide).—This substance was prepared by refluxing 1 g. of the corresponding phthalein with 5 g. of potassium hydroxide and 4 g. of dimethyl sulfate. The red color disappeared and the ether precipitated from the alkaline solution. It was filtered off and crystallized from acetic acid. It formed white needles; m. p., 202°. This was the same substance as that formed in the condensation of 3,6-dimethoxyphthalic anhydride with o-cresol methyl ether.

Analyses. Subs., 0.0808: CO_2 , 0.2115; H_2O , 0.0433. Calc. for $C_{26}H_{26}O_6$: C, 71.99; H, 5.99. Found: C, 71.37; H, 5.95.

1-Hydroxy-2-methyl-5,8-dimethoxy-anthraquinone (VII).—This was prepared from 3,6-dimethoxy-2-(2-hydroxy-3-methylbenzoyl)benzoic acid, sulfuric acid and boric acid in the same way as was the 1-hydroxy-4-methyl-5,8-dimethoxy-anthraquinone (IX). It was recrystallized from glacial acetic acid, giving red needles; m. p., 165°. Its solution in alkali was red; in concd. sulfuric acid it was blue to blue-red, depending on the concentration.

Analyses. Subs., 0.0360: CO₂, 0.0910; H_2O , 0.0162. Calc. for $C_{17}H_{14}O_5$: C, 68.45; H, 4.69. Found: C, 68.43; H, 5.00.

1,5,8-Trihydroxy-2-methyl-anthraquinone (X).—This was prepared from the ether in the same manner as 1,5,8-trihydroxy-4-methyl-anthraquinone (XII) was prepared from its ether. It was purified from glacial acetic acid, forming red needles that sublimed at 250–60°. It dissolved in alkali with the development of a red, and in coned. sulfuric acid to give a blue-red solution.

Analyses. Subs., 0.1153: CO₂, 0.2821; H₂O, 0.0385. Calc. for C₁₅H₁₀O₅: C, 66.66; H, 3.70. Found: C, 66.74; H, 3.71.

2,5,8-Trihydroxy-1-methyl-anthraquinone (XIII).—A solution of 3 g. of o-cresol-3,6-dimethoxy phthalein (IV) and 1.5 g. of 3,6-dimethoxy-phthalic anhydride in 60 cc. of coned. sulfuric acid was heated for 40 hours in a bath at 125°. The anthraquinone (1 g.) was precipitated by pouring the solution into water and purified by precipitation from alkaline solution by carbon dioxide. It was recrystallized from chloroform, forming dark red needles; m. p., 270°. It was identical with the anthraquinone obtained by condensing 3,6-dimethoxy-phthalic anhydride with o-cresol methyl ether, dehydrating the benzoyl-benzoic acid thus obtained, and demethylating the anthraquinone. The substance dissolved in alkali and in coned. sulfuric acid to give a bluish red solution.

Analyses. Subs., 0.0795: CO₂, 0.1935; H_2O , 0.0255. Calc. for $C_{16}H_{10}O_6$: C, 66.68; H, 3.70. Found: C, 66.38; H, 3.58.

m-Cresol Derivatives. 3,6-Dimethoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic Acid (II).—A mixture of 20 g. of dimethoxy-phthalic anhydride, 40 g. of aluminum chloride, and 120 cc. of m-cresol, after standing for 2 hours, was heated for 12 hours in a bath at 75° with mechanical stirring. The products were worked up as in the analogous p-cresol condensation. The yield of crude benzoyl-benzoic acid was 15 g. (50%), and of phthalein, 17 g.

On recrystallizing the crude benzoyl-benzoic acid from methyl alcohol, two substances were obtained. The least soluble fraction formed white needles that melted at 233° and proved to be the above-mentioned substance.

Analyses. Subs., 0.0933: CO₂, 0.2204; H₂O, 0.0450. Calc. for C₁₇H₁₆O₆: C, 64.59; H, 5.66. Found: C, 64.44; H, 5.35.

Subs., 0.3767: required, 1.19 cc. of N NaOH. Calc.: neutr. equiv., 316. Found: 314.

3-Hydroxy-6-methoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic Acid.—A second, much more soluble substance was obtained from the filtrates in the crystallization of

the crude benzoyl-benzoic acid. This when pure melted at 147° (uncorr.) losing water and resolidifying. A second melting point was reached at about 179°. It was impossible to remove all the water by heating the substance at 120°. At 140° for 48 hours the water was removed completely and the product then melted at 187°. This was analyzed and shown to be a monomethyl ether. It probably has the structure assigned it, but this was not proved.

Analyses. Subs., 0.0557, 0.0860: Co_2 , 0.1307, 0.2005: H_2O , 0.0245, 0.0391. Calc. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.63. Found: C, 63.99, 63.57; H, 4.90, 5.02.

Hydrated subs. (m. p., 147°), 0.1468: CO₂, 0.3275, H₂O, 0.0697. Calc. for C₁₆H₁₄O₆.H₂O: C, 60.00; H, 5.00. Found: C, 60.84; H, 5.27.

Hydrated subs. 0.1673: required, 0.529 cc. of N NaOH. Calc.: neutr. equiv., 320. Found: 316.

3,6-Dimethoxy-2-(2-methoxy-4-methylbenzoyl) benzoic Acid.—This substance was prepared from each of the benzoyl-benzoic acids obtained from m-cresol, by the action of alkali and dimethyl sulfate, in a manner similar to the methylation of the analogous o-and p-cresols. The identity of the trimethyl ethers was proved by a mixed melting point. The product forms white needles from methyl alcohol; m. p., 189°.

Analyses. Subs., 0.0668: CO₂, 0.2078; H_2O , 0.0428. Calc. for $C_{18}H_{18}O_6$: C, 65.45; H, 5.45. Found: C, 65.24; H, 5.48.

Subs., 0.5355: required, 1.61 cc. of N NaOH. Calc.: neutr. equiv., 330. Found: 331.

m-Cresol-3,6-dimethoxy-phthalein; (2,2-Bis(4-hydroxy-6-methylphenyl)3,6-dimethoxy phthalein) (V).—This substance was purified in the same way as was 2,2-bis-(4-hydroxy-5-methylphenyl) 3,6-dimethoxy-phthalein (IV). The product formed white needles; m. p., 271°. It is an indicator, the solution changing from colorless to red at $P_{\rm H}$ 9.8. The alkaline absorption spectrum showed a peak at $\lambda 585 {\rm m} \mu$.

Analyses. Subs., 0.0708: CO₂, 0.1843; H₂O, 0.0338. Calc. for C₂₄H₂₂O₆: C, 70.93; H, 5.17. Found: C, 71.10; H, 5.30.

1-Hydroxy-3-methyl-5,8-dimethoxy-anthraquinone (VIII).—A solution of 5 g. of 3,6-dimethoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic acid (II) and 5 g. of boric acid in 100 cc. of 7% oleum was heated for one hour on the steam-bath. The solution was poured over ice and extracted with chloroform. The chloroform solution was washed with sodium bicarbonate solution and again with alkali, which removed the anthraquinone. Acidification precipitated the substance. It was purified from glacial acetic acid, forming red needles; m. p., 172°; yield, about 0.25 g. (6%). Not enough of the substance was obtained to analyze, but it was converted to the corresponding trihydroxy compound (XI).

1,5,8-Trihydroxy-3-methyl-anthraquinone (XI).—The corresponding dimethyl ether (VIII) was refluxed with glacial acetic and hydrobromic acids for 5 hours. As the mixture cooled the trihydroxy compound separated. It was purified from glacial acetic acid, forming red needles; m. p., 227°. The substance dissolved in alkali, giving a blue solution, while the dimethyl ether gave a red solution. Both gave blue-red solutions in concd. sulfuric acid.

Preparation of 3,5-Dimethoxy Phthalic Anhydride. The Acid Barium Salt of 3,5-Disulfo-benzoic Acid.—This substance was prepared by a slight modification of the method of Barth²⁵ and Hohenemser.²⁶ A mixture of 900 g. of benzoic acid, 300 g. of phosphorus pentoxide, and 1500 cc. of 50% oleum was sealed in an iron bomb and heated in an electric furnace for 5 hours at 240-250°. After it had cooled, the bomb was

²⁵ Barth, Ann., 159, 222 (1871).

²⁶ Hohenemser, Ber., 35, 2305 (1902).

3,5-Dimethoxy-2-(4-methoxy-2-methylbenzoyl)benzoic Acid (XVI).—By condensing m-cresol methyl ether with 3,5-dimethoxy-phthalic anhydride, this substance was obtained in 40% yield. It was recrystallized from dil. methyl alcohol, forming white needles; m. p., 233°.

A mixed-melting-point determination showed that this acid is different from the isomer (m. p., 219°) obtained by methylating the compound (XV), indicating that the rule of condensation *ortho* to hydroxyl and *para* to methoxyl groups holds for 3,5- as well as 3,6-dimethoxy phthalic anhydrides.

3,5-Dimethoxy-*m*-cresol-phthalein (2,2-Bis - (4 - hydroxy-6 - methylphenyl)3,5 - dimethoxy Phthalide.—It was found impossible to crystallize this compound free from tarry impurities by the methods used successfully with the other phthaleins.

Attempts at Preparation of Emodin Dimethyl Ether.—A solution of 5 g. of 3,5-dimethoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic acid (XV) and 5 g. of boric acid in 50 cc. of 7% oleum was warmed on the steam-cone for an hour. The anthraquinone was purified as described under the preparation of 1-hydroxy-3-methyl-5,8-dihydroxy-anthraquinone. A very small amount was obtained, sulfonation apparently taking place to a considerable extent. The product crystallized from dil. alcohol in yellow needles; m. p., about 185°. Its solution in alkali was red. This product was refluxed with excess of dimethyl sulfate and alkali for 2 hours. The trimethoxy compound was extracted from the alkaline solution with ether. On evaporation of the ether it was obtained in yellow needles; m. p., about 175–180°. Not enough was obtained to purify. It dissolved in coned. sulfuric acid with the development of a red color. This crude trimethyl ether was used for the absorption spectrum determinations.

Nitration of 3,5-Dimethoxy-2-(2-hydroxy-4-methylbenzoyl)benzoic Acid (XV). 3,5-Dimethoxy-2-(2-hydroxy-4-methyl-5-nitrobenzoyl)benzoic Acid (XIX).—A solution of 4 g. of the benzoyl-benzoic acid in 80 cc. of glacial acetic acid was treated with 1 cc. of nitric acid (sp. gr. 1.42) in 20 cc. of glacial acetic acid at 50-60° for 3 hours. On adding water the nitro acid was obtained in quantitative yield. It was recrystallized from alcohol in light yellow needles; m. p., 241°.

Analyses. Subs., 0.0823: CO₂, 0.1697; H₂O, 0.0325. Calc. for C₁₇H₁₅O₈N: C, 56.51; H, 4.15. Found: C, 56.23; H, 4.38.

Subs., 0.1195: required, 0.642 cc. of N NaOH. Calc.: neutr. equiv., 361, or 180 if the OH were neutralized. Found: 186.

Condensation of 3,5-Dimethoxy-phthalic Anhydride with o-Nitro-m-cresol. 3,5-Dimethoxy-2-(4-hydroxy-2-methyl-5-nitrobenzoyl)benzoic Acid (XVIII).—A mixture of 10 g. of 3,5-dimethoxy-phthalic anhydride, 35 g. of o-nitro-m-cresol, 31 and 20 g. of aluminum chloride was heated and stirred in a bath at 75° for 20 hours. The excess of nitrocresol was steam distilled and the product worked up as before; yield of acid, 9 g. (62%). It was purified from methyl alcohol, forming white needles; m. p., 181°. Only a trace of phthalein derivative was obtained.

Analyses. Subs., 0.1098: CO₂, 0.2299; H₂O, 0.0446. Calc. for C₁₇H₁₅O₈N: C, 56.51; H, 4.15. Found: C, 57.00; H, 4.51.

Subs., 0.1143: required, 0.620 cc. of N NaOH. Calc.: neutr. equiv., 361; or 180 if the OH were neutralized. Found: 184.

Summary

1. A satisfactory method has been developed for the condensation of phthalic anhydride containing methoxyl groups with cresols to form substituted benzoyl-benzoic acids.

³¹ Keller, Ann., 259, 223 (1890).

- 2. 3,6-Dimethoxy-phthalic anhydride was condensed with o-, m- and p-cresols.
- 3. The benzoyl-benzoic acids thus formed were condensed by means of sulfuric acid to the corresponding trihydroxy-methyl-anthraquinones or their ethers.
- 4. The exact structures of the benzoyl-benzoic acid derivatives and of the anthraquinones have been established: first, by comparison with the isomeric bstances (described in the following paper) prepared by condensing 3,6-dimethoxy-phthalic anhydride with cresol ethers; and second, by comparison with the trihydroxy-methyl-anthraquinone of known structure prepared from 3,6-dimethoxy-o-cresolphthalein.
- 5. It has been established that the entering group takes the *ortho* position to the hydroxyl in the cresols.
- 6. The anthraquinones from the benzoyl-benzoic acids derived from o-and p-cresol form readily, and those from the m-cresol only with great difficulty.
- 7. A preliminary study of the condensation of 3.5-dimethoxy-phthalic anhydride with m-cresol and of the formation of the anthraquinone from the resulting benzoyl-benzoic acid derivative has been made, with the object of the synthesis and proof of the structure of the natural drug emodin.
- 8. The course of the condensation of the 3,5-dimethoxy-phthalic anhydride with *m*-cresol was determined by a comparison of the products obtained with this cresol and with *m*-cresol methyl ether and *o*-nitro-*m*-cresol.
- 9. The absorption spectra of the anthraquinones and phthaleins were obtained.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

TRIHYDROXY-METHYL-ANTHRAQUINONES.

By J. H. GARDNER¹ WITH ROGER ADAMS RECEIVED JULY 23, 1923

In the previous paper² a satisfactory method was developed for the condensation of certain phthalic anhydrides containing methoxyl groups with cresols. The resulting benzoyl-benzoic acids were converted to substituted anthraquinones. A detailed study of the condensation of 3,6-dimethoxy-phthalic anhydride with cresols showed that the reactions took place very readily by means of anhydrous aluminum chloride and an excess of cresol as a solvent with the formation of products in which the ketonic carbonyl of the benzoyl-benzoic acid was *ortho* to the hydroxyl group of the cresol. Sulfuric acid in the presence of a little boric acid

¹ This communication is an abstract of a thesis submitted by J. H. Gardner in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Graves and Adams, This Journal, 45, 2439 (1923).

converted the benzoyl-benzoic acids thus formed into the corresponding anthraquinones and these were demethylated to the trihydroxy-methylanthraquinones by means of hydrobromic acid. The benzoyl-benzoic acids were accompanied by diphenyl-phthalide derivatives in the formation of which the condensation took place in the para position to the hydroxyl group of the o- and m-cresol residues and in the ortho position to the hydroxyl group of the p-cresol residue.

In the present work the condensation of 3,6-dimethoxy-phthalic anhydride with the methyl ethers of o-, m- and p-cresol has been studied. The conversion to the corresponding anthraquinone derivatives has been carried out and the structure of the intermediate and final products has been determined.

The initial condensation to the benzoyl-benzoic acids was effected by means of anhydrous aluminum chloride, using an excess of the cresol ether as a solvent. The benzoyl-benzoic acids from o-, m- and p-cresol methyl ethers (I, II and III) were obtained in yields of 24%, 65% and 48%, respectively, as the average of several runs.

In the case of the m-cresol methyl ether, more vigorous conditions were used in the condensation than in the others, thus causing the hydrolysis of one of the ether groups (II).

The acids just mentioned from the o- and p-cresol methyl ethers were accompanied by alkali-insoluble diphenyl-phthalide derivatives (IV and V) in yields of 76% and 21%, respectively. No product of this type formed in the condensation with m-cresol methyl ether, possibly on account of the vigorous conditions used.

The conversion of the benzoyl-benzoic acids into anthraquinone derivatives was first accomplished with the acids from o- and p-cresol methyl ethers (I and III) by heating with concd. sulfuric acid to 150° and cooling immediately with ice. The anthraquinone derivatives thus produced were partially demethylated during their formation.

The benzoyl-benzoic acids were also converted to anthraquinones by heating with concd. sulfuric acid for 20 to 30 minutes at 145–155°. Under these conditions the products were formed and completely demethylated (VI and VIII); this method is, therefore, to be preferred to the other, as a single product is thus obtained.

Such a very small amount of anthraquinone derivative from the acid obtained from *m*-cresol methyl ether resulted from either of the above treatments, that it could not be purified. This is in accord with the results of Weizmann³ and of Graves and Adams² who had difficulty in forming anthraquinones from substituted benzoyl benzoic acids of a similar type.

The structures of the benzoyl-benzoic acids as given (I, II and III) were shown to be correct. Such structures would be expected after a consideration of the work of Nourisson⁴ and Weizmann^{3b} who showed that condensation of phthalic anhydride with phenol ethers took place para to the methoxyl group, providing that position was open. In the first place, the benzoyl-benzoic acids from o- and m-cresol methyl ethers were different from those obtained by the methylation of the benzoylbenzoic acids from 3,6-dimethoxy-phthalic anhydride and o- and m-cresols. The benzoyl-benzoic acid from p-cresol methyl ether was the same as that obtained by the methylation of the condensation product from 3,6-dimethoxy-phthalic anhydride and p-cresol.

Second, the identity of the completely demethylated anthraquinone derivative (VI) from 3,6-dimethoxy-phthalic anhydride and o-cresol methyl ether with that obtained by the condensation of o-cresol-3,6-dimethoxy-phthalein dimethyl ether with 3,6-dimethoxy-phthalic anhydride and sulfuric acid, also shows without question the constitution of the original substance.

³ Weizmann, J. Chem. Soc., (a) 97, 687 (1910); (b) 91, 1626 (1907).

⁴ Nourisson, Ber., 19, 2103 (1886).

Still further proof, and more direct, for the structure of the o-cresol methyl ether compound (I) was obtained. The demethylated anthraquinone (VI) from 3,6-dimethoxy-phthalic anhydride and o-cresol methyl ether was distilled with zinc dust in order to obtain the corresponding methyl anthracene. This, in turn, was oxidized to the methyl anthraquinone and identified as the α -methyl compound. This proves conclusively that the initial condensation must have been para to the methoxyl group in the cresol ether, since if it had been ortho, β -methyl-anthracene would have resulted.

By analogy, it is fair to assume that the *m*-cresol methyl ether also condensed in an analogous way, the ketonic carbonyl going *para* to the methoxyl group. It was mentioned above that the acid was partially demethylated during its formation and it is most probable, judging from the work of Kostanecki and Dreher, that the methoxyl group *ortho* to the ketone carbonyl (II) is the one which has been split.

The constitution of the benzoyl-benzoic acid from p-cresol methyl ether is most certainly that given by Formula III. It is identical with the acid obtained by the methylation of the condensation product of 3,6-dimethoxy-phthalic anhydride and p-cresol.

With the constitution of the benzoyl-benzoic acids fixed, the structures of the anthraquinones formed from them can easily be proved. In the case of the p-cresol methyl ether derivative, only one anthraquinone formula is possible (VIII). The anthraquinone from the o-cresol methyl ether derivative might have one of two formulas (VI or VII), depending upon whether water was eliminated using the hydrogen atom o-rho or p-ara to the methyl group. It has already been mentioned, however, under the discussion of the structure of the benzoyl-benzoic acids, that α -methyl-anthracene could be obtained by reduction of this anthraquinone, thus showing that the hydrogen o-rho to the methyl group has been eliminated and that Formula VI is correct.

It was mentioned that during the formation of the anthraquinones from the benzoyl-benzoic acids under certain conditions partial demethylation took place. From the benzoyl-benzoic acid obtained from o-cresol methyl ether, a monomethylated anthraquinone was formed. The exact structure was not determined, but it seems probable that the product was 2-methoxyl-methyl-5,8-dihydroxy-anthraquinone. The benzoyl-benzoic acid from p-cresol methyl ether yielded an anthraquinone dimethyl ether which was identical with that obtained by Graves and Adams from 3,6-dimethoxy-phthalic anhydride and p-cresol, and so must be 4-hydroxy-1-methyl-5,8-dimethoxy-anthraquinone. This is in accord with the observations of Oesterle who showed that one of the two methoxyl groups in the 1,8-positions in chrysazin is more reactive than the other.

⁵ Kostanecki and Dreher, Ber., 26, 78 (1893).

⁶ Oesterle, Arch. Pharm., 253, 335 (1915).

The structures of the phthalein by-products (IV and V) are correct without doubt. The one formed from the o-cresol methyl ether was the same as that obtained by the methylation of the phthalein obtained by the condensation of 3,6-dimethoxy-phthalic anhydride with o-cresol. In the case of the condensation of the 3,6-dimethoxy-phthalic anhydride with the p-cresol, a fluoran was produced due to the dehydration of the phthalein first formed. When the p-cresol methyl ether was used, no such fluoran formation was possible and the corresponding phthalein was, therefore, produced.

Experimental Part

The 3,6-dimethoxy-phthalic anhydride was prepared as described in the previous paper. The cresol ethers were made by the usual method of treatment of the cresols with sodium hydroxide and dimethyl sulfate.

Condensation of 3,6-Dimethoxy-phthalic Anhydride with the Cresol Methyl Ethers

p-Cresol Methyl Ether Derivatives.⁷ 3,6-Dimethoxy-2-(2-methoxy-5-methylbenzoyl) benzoic Acid (III).—A mixture of 5 g. of 3,6-dimethoxy-phthalic anhydride and 25 cc. of p-cresol methyl ether was prepared in a large Pyrex test-tube provided with a mechanical stirrer. To this was added 15 g. of anhydrous aluminum chloride, and the mixture was stirred continuously for 1 hour so as to give a homogeneous reaction mixture; during this time evolution of hydrogen chloride took place. The tube was then heated for 6 hours at 70°; after 4 to 5 hours the mixture became so thick that it could no longer be stirred.

At the end of the heating the mixture was cooled and slowly treated with 50 cc. of 1:1 hydrochloric acid. The excess of cresol ether was removed by steam distillation, as well as any free cresol which might have formed during the reaction. The residual mixture in the flask was cooled and the dark brown solid was filtered. It was boiled with 10% sodium hydroxide, cooled and filtered. The residue was set aside and the alkaline solution was saturated with carbon dioxide. This caused the precipitation of aluminum hydroxide which was filtered off. From this filtrate $3.5~{\rm g}.~(44\%)$ of 3.6-dimethoxy-2-(2-methoxy-5-methylbenzoyl)benzoic acid was obtained by acidification with hydrochloric acid. It was purified by recrystallization from methyl alcohol and washing with ether, forming colorless, truncated prisms melting at $203-204^{\circ}$.

Analyses. Subs., 0.0812: CO₂, 0.1942; H_2O , 0.0866. Calc. for $C_{15}H_{18}O_6$: C, 65.45; H, 5.45. Found: C, 65.23; H, 5.01.

p-Cresol-3,6-dimethoxy-phthalein Dimethyl Ether, or 2,2-Bis(2-methoxy-5-methyl-phenyl)-3,6-dimethoxyphthalide⁸ (V).—In the preparation of 3,6-dimethoxy-2-(2 methoxy-5-methylbenzoyl)benzoic acid (III) there was always obtained as a by-product a portion insoluble in sodium hydroxide solution. From the reaction mixture described, there was obtained 2.2 g. (21%) of this insoluble material. It was purified by recrystallization from glacial acetic acid, forming colorless needles melting at 187.5°. It was dried to constant weight at 100° before analysis.

Analyses. Subs., 0.0826: CO₂, 0.2164; H₂O, 0.0426. Calc. for $C_{25}H_{26}O_6$: C, 71.89; H, 5.99. Found: C, 71.45; H, 5.73.

⁷ All melting points given in this paper are corrected.

⁸ Nomenclature according to the system used in Chemical Abstracts.

1,5,8-Trihydroxy-4-methyl-anthraquinone.—A mixture of 5 g. of 3,6-dimethoxy-2-(2-methoxy-5-methylbenzoyl)benzoic acid (III) and 100 cc. of concd. sulfuric acid was heated rapidly to 150°. When this temperature was reached the mixture was poured over ice and the dark red precipitate which formed was filtered out. It was dissolved in 10% aqueous sodium hydroxide, the solution filtered and the mixture of anthraquinone derivatives precipitated by means of carbon dioxide; yield, 2.7 g., or 60%. By recrystallization of this crude material from acetone, two fractions were obtained in about equal amounts. The less soluble of these, which proved to be the 4,5,8-trihydroxy-1-methyl-anthraquinone, was recrystallized from glacial acetic acid for further purification. It formed fine red needles, melting at 276–278° with sublimation. It is soluble in concd. sulfuric acid with a blue-violet color, and in alkalies with a violet-red color.

Analyses. Subs., 0.0734: CO_2 , 0.1784; H_2O , 0.0250. Calc. for $C_{15}H_{10}O_5$: C, 66.67; H, 3.70. Found: C, 66.29; H, 3.78.

The more soluble compound obtained from the acetone crystallization proved to be the 1-hydroxy-4-methyl-5,8-dimethoxy-anthraquinone. It was purified further by recrystallization from glacial acetic acid from which it formed long, red needles with a yellowish, metallic gleam. It melted at 224° when pure, dissolved in concd. sulfuric acid with the development of a blue-violet color and in sodium hydroxide to give a bluish-red solution.

Analyses. Subs., 0.0620: CO₂, 0.1566; H₂O, 0.0247. Calc. for C₁₇H₁₄O₅: C, 68.46; H, 4.70. Found: C, 68.89; H, 4.47.

As stated in the introduction, a mixture of products consisting of partially methylated and entirely demethylated anthraquinones by the condensation of 3,6-dimethoxy-2-(2-methoxy-5-methylbenzoyl)benzoic acid (III) and sulfuric acid, could be avoided if the conditions used for the condensation were slightly modified. This latter procedure is to be preferred.

A mixture of $8.5\,\mathrm{g}$. of the benzoyl-benzoic acid and $85\,\mathrm{cc}$. of concd. sulfuric acid was heated at $145-155^\circ$ for 20 minutes. The solution was then poured onto ice, and the precipitate filtered out and redissolved in 10% sodium hydroxide solution. The alkaline solution thus obtained was saturated with carbon dioxide, causing the precipitation of $4.5\,\mathrm{g}$. (65%) of practically pure 4.5.8-trihydroxy-1-methyl-anthraquinone. This was further purified from glacial acetic acid as described above.

o-Cresol Methyl Ether Derivatives. 3,6-Dimethoxy-2-(4-methoxy-5-methylben-zoyl) benzoic acid (I).—A mixture of 5 g. of 3,6-dimethoxy-phthalic anhydride and 20 cc. of o-cresol methyl ether was placed in a large Pyrex test-tube provided with a mechanical stirrer. To this was added 8 g. of anhydrous aluminum chloride and after the mixture had been stirred for an hour it was heated to 65° during a period of 2 hours and continuously stirred, after which it was held at that temperature for 5 hours.

The mixture was cooled and decomposed with 50 cc. of 1:1 hydrochloric acid. The resulting product was treated in exactly the same way as described under the corresponding p-cresol methyl ether derivative. There was thus obtained 1.9 g. (26%) of 3,6-dimethoxy-2-(4-methoxy-5-methylbenzoyl)benzoic acid. It was purified by crystallization from methyl alcohol, then from acetone, and finally dried to constant weight. It was a white powder, melting at 192°.

Analyses. Subs., 0.0934: CO₂, 0.2266; H₂O, 0.0442. Calc. for C₁₈H₁₈O₆: C, 65.45; H, 5.45. Found: C, 66.17; H, 5.26.

o-Cresol-3,6-dimethoxy-phthalein Dimethyl Ether, 2,2-Bis(4-methoxy-5-methyl-phenyl)3,6-dimethoxy-phthalide (IV).—From the condensation just described 8 g. (76%) of the material insoluble in sodium hydroxide was obtained. This was purified by recrystallization from glacial acetic acid, forming colorless needles; m. p., 202-203°.

Analyses. Subs., 0.0808: CO₂, 0.2115; H_2O , 0.0433. Calc. for $C_{26}H_{26}O_6$: C, 71.89; H, 5.99. Found: C, 71.37; H, 5.95.

2-Methoxy-1-methyl-5,8-dihydroxy-anthraquinone.—A mixture of 5 g. of 3,6-dimethoxy-2-(4-methoxy-5-methylbenzoyl)benzoic acid (I) and 100 cc. of concd. sulfuric acid was heated rapidly to 150° and then poured onto ice. The red precipitate was purified as described under the corresponding p-cresol methyl ether derivatives. There was thus obtained 2.5 g. (58% yield) of anthraquinone.

The crude material was recrystallized from glacial acetic acid, forming dark red needles melting at 249–249.5°. From the mother liquors small amounts of 2,5,8-tri-hydroxy-1-methyl-anthraquinone were obtained. The monomethyl ether is soluble in concd. sulfuric acid with the formation of a blue-violet color and dissolved in alkalies to give a blue-red solution.

Analyses. Subs., 0.0823: CO₂, 0.2025; H₂O, 0.0320. Calc. for C₁₆H₁₂O₅: C, 67.61; H, 4.23. Found: C, 67.11; H, 4.32.

2,5,8-Trihydroxy-1-methyl-anthraquinone (VI).—This substance was obtained in small amounts from the mother liquor from the previous condensation, but it was more readily obtained in a pure state by the following procedure.

A mixture of 4 g. of 3,6-dimethoxy-2-(4-methoxy-5-methylbenzoyl)benzoic acid (I), 3 g. of boric acid and 40 cc. of concd. sulfuric acid was heated at 150° for 30 minutes. The solution was poured onto ice, the liquid filtered and the precipitate dissolved in 10% sodium hydroxide solution. After filtration the solution was saturated with carbon dioxide, thus precipitating 1.5 g. (45%) of 2.5.8-trihydroxy-1-methyl-anthraquinone. It was purified by recrystallization from dil. acetic acid and then from chloroform. It formed dark red needles, melting at 270° .

Analyses. Subs., 0.0795: CO₂, 0.1936; H₂O, 0.0255. Calc. for $C_{15}H_{10}O_5$: C, 66.67; H, 3.70. Found: C, 66.38; H, 3.56.

This same substance was obtained by the condensation of 2,2-bis(4-methoxy-5-methylphenyl)-3,6-dimethoxy-phthalide (IV) with 3,6-dimethoxy-phthalic anhydride and sulfuric acid. A mixture of 7 g. of the phthalide with 185 cc. of concd. sulfuric acid and 3.5 g. of 3,6-dimethoxy-phthalic anhydride was heated for 2 days at 125°. The solution was poured onto ice, the dark red precipitate filtered and dissolved in 10% sodium hydroxide solution. By saturating this solution with carbon dioxide, 7.5 g. of the anthraquinone derivative was obtained.

Since the phthalide was formed in large amounts by the condensation of 3,6-dimethoxy-phthalic anhydride with o-cresol methyl ether, this method of preparation of the 2,5,8-trihydroxy-1-methyl-anthraquinone was more satisfactory than that by the dehydration of 3,6-dimethoxy-2-(4-methoxy-2-methylbenozyl)benzoic acid (I).

Conversion of 2,5,8-trihydroxy-1-methyl-anthraquinone (VI) to 1-methyl-anthraquinone.—A sample of 2,5,8-trihydroxy-1-methyl-anthraquinone was reduced to methyl-anthracene by distillation with zinc dust, following the method of Gattermann. The crude material thus obtained was oxidized to methyl-anthraquinone, following the method of Fischer and Reinkober. The product thus obtained was purified by crystallization from dil. acetic acid, forming yellow needles melting at 167°, which is the melting point of 1-methyl-anthraquinone. When this product was mixed with a sample of pure 2-methyl-anthraquinone melting at 174°, the melting point of the mixture was lowered to 154°, indicating that the compounds were not the same.

m-Cresol Methyl Ether Derivatives. 3-Hydroxy-6-methoxy-2-(4-methoxy-1-

⁹ Gattermann, "Practical Methods of Organic Chemistry," MacMillan and Co., 1914, p. 369.

¹⁰ Fischer and Reinkober, J. prakt. Chem., [2] 92, 49 (1915).

methylbenzoyl)benzoic acid (II).—A mixture of 5 g. of 3,6-dimethoxy-phthalic anhydride and 25 cc. of m-cresol methyl ether was condensed in the same manner as the o-and p-cresol methyl ethers with the exception of a few details. The mixture was heated up to 75° during the course of 1.5 hours, and maintained at that temperature for 7 hours. When worked up in the manner previously described, no alkali-insoluble product was obtained but merely 4.9 g. (65%) of a dimethyl ether, probably 3-hydroxy-6-methoxy-2-(4-methoxy-1-methylbenzoyl)benzoic acid (II). This was purified by crystallization from methyl alcohol, forming colorless prisms melting at 194–195°. It was dried to constant weight before it was analyzed.

Analyses. Subs., 0.0766: CO_2 , 0.1806; H_2O , 0.0342. Calc. for $C_{17}H_{16}O_6$: C, 64.56; H, 5.06. Found: C, 64.30; H, 4.67.

Summary

- 1. 3,6-Dimethoxy-phthalic anhydride was condensed with o-, m- and p-cresol methyl ethers.
- 2. The benzoyl-benzoic acids formed from the o- and p-cresol methyl ethers were condensed by means of sulfuric acid to the corresponding trihydroxy-methyl-anthraquinones or their methyl ethers. By varying the conditions of condensation it was possible either to obtain partial demethylation or complete demethylation during this reaction.
- 3. The structures of the benzoyl-benzoic acids obtained were established: first, by comparison with the isomeric substances obtained by the condensation of 3,6-dimethoxy-phthalic anhydride with cresols; and second, by direct proof.
- 4. It has been established that the entering group takes the para position to the methoxyl groups in the o- and m-cresol ethers and the ortho position to the methoxyl in the p-cresol methyl ether.
- 5. The structure of the anthraquinones obtained from the benzoylbenzoic acids was determined.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE YIELDS OF SOME GRIGNARD REAGENTS

By Henry Gilman and Roy McCracken¹ Received July 31, 1923

Introduction

In connection with a series of studies involving the Grignard reagent, it was necessary to determine the approximate yield in the preparation of a number of typical RMgX compounds. A knowledge of such yields is quite indispensable in certain studies. In particular is this true of reactions involving an excess of some compound treated with the Grignard reagent, and when the interpretation of mechanism of such a reaction

¹ This paper is an abstract of a thesis presented by Roy McCracken in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

is in no small way determined by the yields of products. Apart from these immediate considerations, the study is not without some interest in such general problems as steric hindrance and the order of activity of halogens in organic compounds.

The method used for the quantitative estimation of the various compounds was that previously described.² Although no optimum condition was determined for the formation of any of the reagents described in this paper, advantage was taken of the opportunity to incorporate where possible those factors which were found earlier³ to give a maximum yield of ethylmagnesium iodide. It is quite probable that although the quantity of organic halide used was only that which would react theoretically with 1.15 g. of magnesium, the yields determined are such as may be expected, in larger runs made under comparable conditions. In this connection a quantitative study of yields, when the commonly used solvent (ether) is replaced in large part by other more desirable solvents such as benzene, is in progress. Here the method of analysis by titration will be checked in part by the preparation of standard compounds in fairly large quantities.

Procedure

The technique was essentially identical with that previously described in determining the best conditions for the preparation of ethylmagnesium iodide.³ In each run 1.25 g. of magnesium turnings was used, and the weight of halide taken was approximately that which would theoretically react with 1.15 g. of magnesium. A small crystal of iodine was added in each run as a catalyst; the halide in ether was added over a 45-minute period, and stirring was used throughout.

With a few of the compounds (the bromotoluenes, β -bromostyrene, and α -bromonaphthalene) which react with magnesium rather sluggishly at first, a minor alteration in procedure was made. Instead of adding 25 cc. of ether to the magnesium before the addition of the halide, only about 3 cc. was run in and then about 2 cc. of the ether solution of halide. This mixture was warmed until the reaction set in, and then the remainder of the ether solution of halide was added over 45 minutes.

Duplicate runs were made on each compound, and from each run two samples were removed for analysis. The yields given in the following table are, therefore, average yields for at least 4 analyses. Because of the apparently unusual results observed with some of the compounds, repeated check determinations were made up to 12 and 16 analyses. The agreement in results was of the order already noted: 3 very few of the analyses varied from the average by more than 1%, and practically all were within 0.5% of the average.

² Gilman, Wilkinson, Fishel and Meyers, This Journal, 45, 150 (1923).

³ Gilman and Meyers, ibid., 45, 159 (1923).

TABLE I RESULTS

Halide used	Av. % yield of corres. organomagn hal.		Av. % yield of corres. organomagn, hal.		Av. % yiel of corres. organomage hal.	
n-Propyl iodide.	. 79.35	n-Butyl bromide.	91.23	$o ext{-Bromotoluene}$	86.6	5
n-Butyl iodide	. 65.23	iso-Butyl bromid	e 78.23	m-Bromotoluene	84.7	5
n-Amyl iodide	. 75.76	sec-Butyl bromid	e 68.26	p-Bromotoluene	88.1	6
n-Hexyl iodide	. 59.50	tert-Butyl bromid	e 20.62	Benzyl chloride	94.2	8
n-Heptyl iodide.	. 64.27	n-Butyl chloride.	87.38	α-Bromonaphthale	ne. 70.5	0
n-Octyl iodide	. 44.22	Bromobenzene	94.37	Bromocyclohexane	68.3	2
Lauryl bromide.	. 73.70	Iodobenzene	84.58	β -Bromostyrene	47.5	9

With n-butyl iodide a first pair of duplicate runs gave an average percentage yield of 78.24. Because it was felt early in the work that the yield should have been nearer to those with n-butyl bromide and n-butyl chloride, a check determination was made on a more highly purified sample. This second pair of duplicate runs averaged more than 10% lower. This necessitated another determination, and to avoid any uncertainty a third and a fourth pair of duplicate runs were made. The second, third and fourth runs agreed quite closely and the average of these three runs (12 analyses) is that given, 65.23%. Although the percentage obtained in the first determination fits in admirably with the drop in yield with increasing length of carbon chain, it should be discarded.

In the cases of n-hexyl iodide, lauryl bromide and bromocyclohexane a pair of duplicate runs was made and the result for each is the average of 8 analyses.

n-Butyl chloride showed no evidence of a reaction with magnesium until after three hours of stirring. In sequence, each reaction mixture was stirred for 4 hours, then allowed to stand for 8 hours, and finally stirred for 4 hours.

The percentage listed for benzyl chloride is an average of a pair of duplicate runs. In another determination, where the benzyl chloride was used directly without special purification by drying and by distillation, the yield was 4% less.

All halides were purified at least by a combination of drying and distillation, with the exception of the butyl bromides, butyl chloride, and the bromotoluenes. These were used directly from small stock bottles, and were of the regular high grade quality to be had from American houses.

Discussion

The yields of organomagnesium halides prepared from normal alkyl iodides confirm in large part several observations to be found in the literature. It has long been known that the yield of Grignard reagent drops with the increasing length of the carbon chain, and that probably the concurrent Wurtz reaction becomes more prominent.

Two interruptions to an orderly decrease, however, are to be noted with *n*-butyl and *n*-hexyl iodides. Several check analyses with highly and freshly purified samples failed to alter appreciably the average percentages indicated. If an explanation for this apparent irregularity is sought in the phenomenon of alternating properties of even and odd numbered members of an homologous series, it must be remembered that the yield of ethylmagnesium iodide, determined scores of times, has always been considerably higher than that of *n*-propylmagnesium iodide.

The yields of the 4 butylmagnesium bromides indicate in a striking

fashion that the increasing complexity of branching of an alkyl group runs parallel with a decrease in yield of the corresponding organomagnesium halides.

The three bromotoluenes show comparatively small differences.

A comparison of yields of several of the compounds reveals the desirability of using bromides instead of iodides where the bromides are not too volatile and where there is not too much difficulty in initiating a reaction with magnesium. First, n-butyl bromide gives a decidedly larger yield of the corresponding organomagnesium compound than does n-butyl iodide. Second, the yield of phenylmagnesium bromide is significantly larger than that of phenylmagnesium iodide. Third, it is quite obvious that if the regular decrease in yield with normal alkyl halides extends to the higher members of a series, the yield of laurylmagnesium bromide far exceeds what one might expect for laurylmagnesium iodide.

In this connection the yield of n-butylmagnesium chloride is noteworthy. It is considerably larger than that of n-butylmagnesium iodide and only slightly smaller than that of the corresponding bromide. There is a possibility that it might exceed the yield of bromide if the reaction with magnesium could be made to start more easily. This point is to be tested in connection with some studies on the activation of reagents used in the preparation of organomagnesium compounds. There is undoubtedly a limiting factor here when one compares the halogen attached to like radicals, because work recently published and studies now being carried on in this Laboratory point strongly to decidedly poor yields of organomagnesium fluorides, whenever it is possible to prepare them at all.

The yield of benzylmagnesium chloride is surprisingly high. For this reason it was checked and re-checked. The literature contains many references to the rather large quantity of dibenzyl formed by the usual Wurtz-Fittig reaction which apparently accompanies all preparations of the Grignard reagent. It is highly probable, therefore, that the conditions for an optimum yield of ethylmagnesium iodide which have been extended to the compounds mentioned in this study might, for the present, be advantageously used in the preparation of all Grignard reagents.

The yields of the last three compounds listed were determined because they are typical of some classes of substances frequently used in synthetic work.

Summary

The yields of a number of typical Grignard reagents have been determined, and attention has been directed to some apparent regular-

⁴ The observations on chlorides should be restricted to alkyl chlorides, for although it is possible to prepare phenylmagnesium chloride directly the reaction is unusually sluggish and the yield such as to make the preparation essentially without value.

⁵ Swarts, Bull. soc. chim. Belg., 30, 306 (1921).

ities underlying the correlation of yield with the kind of organic halide used.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]
THE FORMATION OF FREE RADICALS BY REDUCTION WITH
VANADOUS CHLORIDE

Preliminary Paper

By J. B. Conant and A. W. Sloan Received August 3, 1923

The addition of vanadous chloride to a solution of triphenylpyrylium chloride (I) causes the formation of a reddish precipitate which can be obtained in a fairly pure condition by filtering in an atmosphere of carbon dioxide. This colored, insoluble substance behaves like a free radical; a chloroform solution of it is bright red and the color disappears when the solution is shaken with air. The substance is reoxidized to the pyrylium salt by ferric chloride; if this process is carried out quantitatively in the absence of oxygen a maximum of one molecule of ferric chloride is required. Considerably less than this amount suffices to oxidize a precipitate which has stood for some hours even in an atmosphere of carbon dioxide; the compound is apparently unstable.

While these facts clearly indicated that we were dealing with a free radical, we desired to obtain still more positive evidence. We, therefore, investigated the reduction of the salts of phenylxanthenol (II) from the chloride of which Gomberg¹ obtained the free radical phenylxanthyl by the action of metals in benzene solution. Phenylxanthenol dissolves to a slight extent in coned. hydrochloric acid, producing an orange-colored solution. This solution presumably contains a chloride for which the oxonium formula (III) can be written. This salt is much more readily hydrolyzed than the pyrylium salt, so that it is necessary to work with coned. hydrochloric acid solutions. When such a solution of phenyl-xanthylium chloride is treated with vanadous chloride a brown precipitate

$$\begin{array}{c|c} C - C_{e}H_{5} \\ \hline C + CH \\ C \\ C_{b}H_{5} - C \\ \hline C \\ C - C_{e}H_{5} \\ \hline C \\ CI \\ \hline (I) \\ \hline \begin{pmatrix} C_{e}H_{4} \\ C_{e}H_{4} \\ C \\ C_{e}H_{4} \\ C \\ C_{e}H_{5} \\ C_{e}H_{5} \\ C \\ C_{e}H_{5} \\ C \\ C_{e}H_{5} \\ C \\ C_{e}H_{5} \\ C_{e}H_{5} \\ C \\ C_{e}H_{5} \\ C \\ C_{e}H_{5} \\ C \\ C_{e}H_{5} \\ C_{e}H_{5} \\ C \\ C_{e}H_{5} \\ C \\ C_{e}H_{5} \\ C \\ C_{e}H_{5} \\ C_{e}H_{5} \\ C \\ C_{e}H_$$

¹ Gomberg and Cone, Ann., 370, 154 (1909).

is formed which is very similar in its reactions to the substance formed by the reduction of triphenylpyrylium chloride. It dissolves in chloroform or benzene giving a red solution which to the eye seems identical with solutions of phenylxanthyl (IV) prepared according to Gomberg's procedure. Furthermore, on shaking these solutions with air a peroxide is formed identical with the peroxide formed by oxidation of phenylxanthyl. There is, therefore, no doubt that vanadous chloride reduces phenylxanthylium chloride to phenylxanthyl, and there is every reason to believe that from triphenylpyrylium chloride a corresponding free radical is formed.

This novel type of reduction is not confined to oxonium salts. The so-called carbonium salts of triphenylcarbinol are reduced by vanadous salts to triphenylmethyl. Triphenylcarbinol is slightly soluble in a very concentrated aqueous solution of zinc chloride saturated with hydrogen chloride; a colored precipitate is formed on adding vanadous chloride to this solution. The existence of triphenylmethyl in this precipitate was demonstrated both by the color of a benzene solution and by the isolation of the peroxide obtained on shaking the solution with air. A solution of triphenylcarbinol in concd. sulfuric acid is also reduced by vanadous chloride, a precipitate containing triphenylmethyl being formed.

In this preliminary paper we shall not enter into a discussion of the much debated subject of the constitution of salts of triphenylcarbinol² nor of the relative advantages of the oxonium or carbonium formulas for the pyrylium and xanthylium compounds.³ For our present purposes we may consider that *in solution* the "oxonium" and the "carbonium" salts are present, at least to some extent, as polar compounds; if this is so, the reduction of such salts to free radicals is comparable to the reduction of stannous chloride to metallic tin by the action of chromous chloride. These processes appear to be reversible and to consist essentially of the gain or loss of an electron from a certain group of atoms which can function either as a positive ion or as a free radical, thus: $(C_6H_5)_3C^+ + E$ $C_6H_5)_3C^-$.

Recent investigations have shown that a number of reversible organic processes which can be formulated in terms of electronic transfer give definite potentials.⁴ Preliminary experiments indicate that reduction potentials of certain organic salts to free radicals can also be measured; such potentials of free radicals are analogous to the single potentials of

² See Hantzsch [Ber., 55, 953 (1922)] for one of the recent papers on this subject.

³ Gomberg and West, This Journal, 34, 1529 (1912). Gomberg and Cone, Ann., 376, 183 (1910).

⁴ (a) Haber and Russ, Z. physik. Chem., 47, 257 (1904). (b) Granger and Nelson, This Journal, 43, 1401 (1921). (c) Clark, J. Wash. Acad. Sci., 10, 255 (1920). (d) Billmann and Lund, Ann. chim., 16, 321 (1921). (e) Conant, Kahn, Fieser and Kurtz, This Journal, 44, 1382 (1922). (f) LaMer and Baker, ibid., 44, 1954 (1922). (g) Conant and Fieser, ibid., 44, 2480 (1922).

the metals. We hope to deal with this subject in more detail in another paper.

Free Radicals and Bimolecular Reduction

The extensive work of Gomberg and others on free radicals has shown that the so-called free radical is in solution an equilibrium mixture of the monomolecular free radical and its bimolecular association product. In the case of triphenylmethyl the following equation represents one of the equilibria which are involved (we will neglect in this discussion the tautomeric equilibria involving color changes). $2(C_6H_5)_3C^- \longrightarrow (C_6H_5)_3C^ C(C_6H_5)_3$. The extent of the dissociation of the bimolecular form is a function of the nature of the groups attached to the central carbon atom. This being the case, one would expect that in many cases in which "onium halides" were reduced to radicals the free radicals would polymerize completely to the associated form; if this associated form was not appreciably dissociated in the solution, simple bimolecular reduction would apparently have occurred. However, if the first reduction product should separate rapidly in the solid form before it had wholly associated it might be possible to obtain a solid "free" radical whose existence in solution could not be demonstrated. We believe that we have realized such a case in the reduction of the salts of xanthenol (V) with vanadous chloride. When a very dilute solution of xanthenol in concd. hydrochloric acid is treated in the cold with vanadous chloride a pink precipitate is immediately formed. This can be filtered off and is stable for a few hours in the air but gradually becomes colorless. The colorless solid is bixanthyl⁵ (VI).

$$O \xrightarrow{C_6H_4} CHOH \qquad O \xrightarrow{C_6H_4} CH-CH \xrightarrow{C_6H_4} O$$

$$(VI) \qquad (VII)$$

bright pink precipitate is washed with water, sucked dry and then dissolved in chloroform in the absence of air (in a special apparatus) a momentary color is produced in the chloroform which fades in a few seconds. The chloroform solution on evaporation yields bixanthyl. This color change is a strong indication that the solid which is precipitated on the addition of vanadous chloride contains some "free" xanthyl radical (VII) which dissolves in chloroform with a brown color and then immediately and completely polymerizes to the colorless bixanthyl. If our interpretation of these color changes is correct a new method is available for mak-

⁵ Fosse, Bull. soc. chim., [3] 35, 1005 (1906).

ing solid organic radicals which are not free in solution. We are now investigating the extension of this method as well as the closely allied problem of the reduction of various types of aldehydes and ketones with vanadous and chromous salts.

The reduction of pyridinium and acridinium salts should be entirely analogous to the reduction of pyrylium and xanthylium compounds. Indeed, Cone showed some years ago that by the action of metallic zinc on an aqueous solution of N-phenyl-phenylacridinium chloride a free radical was formed. This reaction can be formulated either as the general reaction between a metal and the solution of an organic chloride giving a free radical or as a case of reduction brought about in this case by a metallic reducing agent. There is one difference between the reduction of pyrylium and pyridinium compounds: the reduction products of the former series whether as free radicals or in the bimolecular form no longer have basic properties; they therefore precipitate from acid solution on the addition of vanadous chloride. This would not be the case with the nitrogen compounds, since even in the reduced form the trivalent nitrogen would have basic properties. It is, therefore, not surprising that on the addition of vanadous chloride to benzylpyridinium chloride (VIII) there is no apparent change; on making the solution alkaline, however, and extracting with ether, the bimolecular reduction product, N',N-dibenzyl-tetrahydrodipyridyl (IX), is obtained. By analogy with the carbonium compounds

there is every reason to believe that the first step in the process is the formation of the free radical, benzylpyridinium, but since this is soluble in the acid solution it immediately polymerizes to the bimolecular form.

If we formulate the relationship between a free radical and the corresponding "onium salt" in terms comparable to the single electrode potential of a metal, it is obvious that all reducing agents whose potentials are below the potentials of the free radicals should cause the precipitation of the radical. In the case of those compounds which we have so far investigated, vanadous chloride has a sufficiently low potential (normal potential about —0.200 referred to hydrogen) to cause this reaction; titanous salts (about —0.040) do not cause a rapid reduction. Chromous

6 Cone, This Journal, 34, 1695 (1912); 36, 2101 (1914).

⁷ Weitz, [Ann., 425, 202 (1921)] and Emmert [Ber., 53, 370 (1920)] reported that they had obtained this free radical, but later [Ber., 55, 2322, 2864] showed conclusively that the colored substance was bimolecular.

chloride (—0.400) reduces the substances in question to free radicals just as does vanadous chloride, but because of its relative stability we have preferred to use the latter reagent. If too powerful a reducing agent be employed in such a process the free radical may be further reduced to the hydrogen compound, just as arsenic and antimony may be reduced to their hydrides. As in inorganic chemistry, the solubility and dissociation of the various factors and products in an electrochemical reaction are quite as important as the value of the normal potentials. Until we have such information, together with the potentials of the free radicals, it is profitless to pursue further the electrochemical aspects of these reactions.

Experimental Part

Reduction of 2,4,6-Triphenylpyrylium Chloride.—The ferric chloride double salt of this chloride was prepared according to the method of Dilthey⁸ and from it the pseudo base and the iron-free chloride. Both the chloride and the ferric chloride double salt are reduced by vanadous chloride in the same manner, except that with the latter compound a certain amount of vanadous chloride is used up in reducing the ferric to ferrous salt. Because the ferric salt is more conveniently prepared it was used in most of the experiments of which the following is typical.

One g. of the ferric chloride double salt was dissolved in 125 cc. of air-free water in a 200cc. Erlenmeyer flask. The flask was swept out with carbon dioxide and 0.1 N vanadous chloride added from a buret while the flask was constantly shaken. A reddish solid soon began to precipitate; vanadous chloride was added in excess (until no further precipitate formed). The mixture was then filtered through a Gooch funnel in an atmosphere of carbon dioxide and washed with air-free water.

The red-brown solid thus obtained dissolved in chloroform or benzene with a red color; when shaken with air the solution became colorless or yellow. When suspended in water and treated with ferric chloride solution the brown solid went into solution rapidly and the characteristic yellow double salt of pyrylium chloride and ferric chloride separated on the addition of hydrochloric acid. Several attempts to dry the precipitate in an atmosphere of carbon dioxide were unsuccessful, either because of failure to exclude air completely or because the compound slowly decomposed; the resulting solid was a mixture of yellow and blackish materials which did not show the characteristics of the original compound.

A number of quantitative experiments were carried out in which the precipitate after it was washed was oxidized with ferric alum in an atmosphere of carbon dioxide either with or without the addition of a little benzene to facilitate the solution. After the solution had been thoroughly shaken for 5 minutes the excess of ferric salt was titrated with standard titanium chloride using ammonium thiocyanate as an outside indicator. The following summarizes the results which are very variable but indicate

⁸ Dilthey, J. prakt. Chem., 94, 65 (1916).

that one equivalent of hydrogen is involved as a maximum. The figures represent moles of ferric salt required to oxidize the precipitate formed from one mole of double salt: (1) freshly precipitated, 0.92, 0.74, 0.59, 1.00; (2) after 14 hours in carbon dioxide, 0.50; (3) after 3 days in carbon dioxide, 0.29.

Reduction of 9-Phenylxanthylium Chloride.—Half a gram of 9-phenylxanthenol was dissolved in 20 cc. of concd. hydrochloric acid and 5 cc. of water by gently warming the mixture. The resulting orange-colored solution was cooled, filtered from a very small amount of insoluble material by means of glass wool and placed in a separatory funnel filled with carbon dioxide. An excess of 0.1 M vanadous chloride was run in and a brown precipitate was immediately formed. Chloroform (about 20 cc.) was then added and the mixture shaken; the heavy precipitate completely dissolved, imparting a deep red color to the chloroform. This solution was then run into another vessel and shaken with air; the color rapidly vanished. On evaporation of the chloroform a white solid was obtained which was freed from a small amount of oily material by washing it with ether. It melted sharply with decomposition at 208–209° and weighed 0.25 g. Recrystallized from benzene, it melted at 211° and was identified as phenylxanthyl peroxide by comparison with a sample prepared according to Gomberg's procedure.

Reduction of Triphenylcarbinol.—A solution of 0.2 g. of triphenylcarbinol in a mixture of 5 cc. of coned. hydrochloric acid and 10 cc. of zinc chloride solution (100 g. in 50 cc. of water) saturated with hydrogen chloride at a temperature of 70-80°, was cooled and filtered through glass wool; vanadous chloride was added to it in an atmosphere of carbon dioxide. A reddish precipitate was formed which was rapidly filtered off and dissolved in benzene in the absence of air. A brown solution was formed, the color of which was discharged by shaking with air. The benzene solution on spontaneous evaporation yielded a small amount of white solid, insoluble in ether, which melted sharply to a red melt at 180-182° (triphenylmethyl peroxide melts at 185-186°). A solution of 0.5 g. of triphenylcarbinol in 20 cc. of 95% sulfuric acid was treated with vanadous chloride solution; a red precipitate formed. The evolution of hydrogen chloride somewhat hindered the carrying out of this reaction; we propose to use vanadous sulfate for such reactions in future work. The sulfuric acid suspension of the reddish precipitate was poured onto cracked ice and the mixture filtered as soon as the ice had melted. The precipitate dissolved in benzene with the development of color; the color disappeared when the solution was shaken with air and the peroxide was obtained by evaporating the benzene solution and treating the residue with ether.

Reduction of Xanthylium Chloride.—A solution of 2 g. of xanthenol in 50 cc. of concd. hydrochloric acid saturated with hydrogen chloride at 0° was filtered from a small amount of material by passing it through glass wool. The light brown solution was treated with an excess of vanadous chloride in the usual manner and the resulting precipitate rapidly filtered in the air and washed with water. A pink solid was thus obtained; attempts to dry it in nitrogen without loss of color were unsuccessful. Recrystallized from acetone after it had become colorless it yielded 1.3 g. of bixanthyl⁵ (m. p., 204–205°) and 0.2 g. of oily material. In another experiment the precipitate was immediately dissolved in chloroform, the chloroform solution showing a faint red color for a few seconds and then becoming colorless. Bixanthyl was obtained in a good yield from this solution. To ascertain whether or not the rapid fading of the color of the solution was due to oxidation, the solution in chloroform was carried out in the absence of air. Some of the freshly precipitated compound was placed in one leg of a wide Y-tube and chloroform placed in the other leg. The apparatus was then repeatedly evacuated and filled with nitrogen (free from oxygen). The tube was then tilted and the chloroform

rapidly run onto the precipitate which dissolved with a momentary red color, forming after a few seconds a colorless solution. This is strong evidence that the color change was not due to oxidation but to polymerization.

Reduction of Benzylpyridinium Chloride.—A solution of 2 g. of benzylpyridinium chloride in 50 cc. of water was treated with 50% more than the amount of vanadous chloride equivalent to two hydrogen equivalents. No precipitate formed but the vanadous chloride was evidently oxidized, as the first portion of it rapidly changed color. The solution was made strongly alkaline and the solution containing a suspension of inorganic hydroxides and organic material was repeatedly extracted with ether. On evaporation a brown solid was obtained which on washing with alcohol became nearly white. It melted at 74-83° and was identified as N,N'-dibenzyl-tetrahydro-dipyridyl by the very characteristic blue color which its alcoholic or acetone solutions acquired when warmed in air.

Summary

- 1. Vanadous chloride reduces triphenylpyrylium chloride, forming a colored substance insoluble in water that behaves like a free radical. The same reagent reduces phenylxanthylium chloride to the free radical, phenylxanthyl, previously prepared by Gomberg.
- 2. Triphenylcarbinol in concd. hydrochloric acid or sulfuric acid solution is reduced to triphenylmethyl by vanadous chloride.
- 3. Xanthenol in concd. hydrochloric acid is reduced by vanadous chloride to bixanthyl. The color of the product indicates that a free radical is first formed which is stable only in the solid state. Benzylpyridinium chloride is reduced to a bimolecular product; no insoluble compound is formed in contrast to the behavior of the oxonium and carbonium chlorides.

CAMBRIDGE 38, MASSACHUSETTS

NEW BOOKS

The Theory of Allotropy. By A. Smits, Ph.D., Professor of Chemistry in the University of Amsterdam. Translated from the German with the Author's sanction by J. Smeath Thomas, D.Sc., Senior Lecturer on Chemistry in the University of Liverpool. (Text-Books of Physical Chemistry, edited by Sir William Ramsay and F. G. Donnan.) Longmans, Green and Company, 55 Fifth Avenue, New York; London, Toronto, Bombay, Calcutta and Madras; 1922. xiii + 397 pp. 239 figs. 22 × 14 cm. Price \$7.00 net.

Many of the writers of scientific papers published in the Netherlands seem tacitly to assume that the reader is thoroughly familiar with the writer's previous papers and can therefore without explanation apprehend the precise meaning of terms and symbols. In a series of papers this may be unavoidable, but a book made from them should surely include a fundamental discussion comprehensible to the reader not already a specialist in the topic. American readers of this book will find the explanatory matter inadequate, and the general mode of treatment is not attractive enough to persuade many of them to proceed far with the task of reading

it comprehendingly. Part of the difficulty is inherent in the subject; but the drier the subject, the more care must one take in exposition. The first two pages are designed to set forth the basis of the theory, but do it so curtly that to many readers they would convey little. On the third page the author plunges into his subject and devotes about half of the book to a theoretical discussion of various possible cases, using the methods of Gibbs, which are more familiar to Hollanders than to Americans. In the latter half he takes up a number of cases which have been investigated experimentally and considers the application of the theory to account for electrochemical phenomena, passivity of metals in particular. The essence of the theory is that allotropy is a case of tautomerism; that an allotropic substance, though in many respects it behaves as a one-component system, is in reality a mixture of two molecular species or pseudocomponents which in general are in equilibrium with each other. This hypothesis is very helpful in accounting for the phenomena observed in systems such as sulfur where the observed melting temperature, for instance, depends upon the previous history of the sample of sulfur; but there is a question as to how far one is practically justified in extending it to all of the cases to which the author applies it. To the student specifically interested in the subject of allotropy the book will be welcome, but it cannot be commended to any other class of readers.

JOHN JOHNSTON

Anorganische Chemie: ein Lehrbuch zum Weiterstudium und zum Handgebrauch. (Inorganic Chemistry: a textbook for the more advanced student and for reference.) By Dr. Fritz Ephraim, Professor at the University of Berne. Second and third editions, revised. Theodor Steinkopff, Residenzstr. 12 b, Dresden-Blasewitz, 1923. viii + 742 pp. 55 figs. 24.5 × 16.5 cm. Price unbound \$2.00; bound \$2.40.

It is not surprising that a third edition of this excellent handbook has been required. In it, account has been taken of the most recent advances in this field, and numerous minor improvements have been made. The book is, however, substantially unchanged from the first edition.

It is too bad that so good a book as this is printed on such miserable paper.

ARTHUR B. LAMB

Laboratory Exercises in Inorganic Chemistry. By James F. Norris, Professor of Organic Chemistry, Massachusetts Institute of Technology, and Kenneth L. Mark, Professor of Chemistry, Simmons College. International Chemical Series, H. P. Talbot, Ph.D., Consulting Editor. McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York; 6 and 8 Bouverie Street, E. C. 4, London, 1922. x+548 pp. 16 figs. 21 × 14 cm. Price \$2.00.

This book is intended for "the student who has had a good training in Chemistry in the high school, and who should have his interest stimulated in his college course, and should be given an opportunity to extend his experience." In carrying out this purpose, the authors have avoided the mere repetition of the more purely illustrative experiments performed in the high school, and have introduced a large number of experiments to emphasize the general principles of chemistry, as the following titles of the first 20 experiments will show.

Physical and Chemical Changes; Mixtures and Pure Substances, (an important topic often slurred in elementary courses); Oxygen; Hydrogen; Quantitative Studies of Chemical Reactions; Water; Chlorine; Hydrochloric Acid; Hydrogen Peroxide; Properties of Liquids and Solids; Carbon and Its Compounds; Acids, Bases, and Salts; Solutions; Chemical Equilibrium; Sulfur and Sulfides; Oxides and Acids of Sulfur; Nitrogen and the Atmosphere; Ammonia; Acids and Oxides of Nitrogen; Atomic and Molecular Weights. The experiments which follow take up Groups 7 and 5, organic compounds, silicon and boron, and then the metals, but include also experiments on the physical properties of the metals, chemical properties of the metals, and electrochemistry. Each assignment is preceded by a discussion which should enable the student to understand the general purpose of the experiments. The experimental directions are clear, and involve simple apparatus.

The most striking feature of the book is the list of questions upon each experiment. The authors have resisted the temptation to do all the thinking for the student by wording the questions so as to indicate the answer. The questions are, on the contrary, well calculated to stimulate the student to accurate observation and clear reasoning. In the opinion of the reviewer, this course represents a noteworthy effort to give the student the proper foundation for the understanding of modern chemistry.

TOEL H. HILDEBRAND

Die Physikalische Chemie in der Inneren Medizin (Physical Chemistry as Applied to Internal Medicine). By Prof. Dr. H. Schade, Director of the Physico-chemical Division of the Medical Clinic, University of Kiel. Theodor Steinkopff, Dresden and Leipzig. 1921. vii + 569 pp. 107 figs.

The development of physical chemistry as an independent entity has determined great progress in many fields of thought. Among these, the medical sciences upon which the art of healing is based, have been notably stimulated and expanded by the application of these concepts and generalizations. Recognizing the import of scientific development to the practice of the art, the author has prepared a non-mathematical summary for the use of physicians and students. The introductory chapters are devoted to an exposition of certain fundamental concepts in the physico-chemical field. In the main the facts are clearly presented, at times, excellently, and the summary solution of certain of the still disputed questions of theory will probably not prove disquieting to the author's prospective

clientele. As an example may be cited the author's opening sentences (p. 2) in which solutions are divided into three "sharply defined" types. From time to time, the author pauses to emphasize the validity of purely materialistic concepts. One wonders why his optimistic prophecy concerning cell morphogenesis is not supported by quotation from Bastian's ingenious—and meaningless—experiments. The major portion of the volume is concerned with the principal thesis, the pathological conditions discussed being arranged chiefly in a topographical classification. The blood, alimentary canal, liver, kidneys, lungs, circulatory and nervous systems, are among the topics treated. It is to be regretted for the authority of the book that the access of the writer to literature other than that in German, was so limited. While the disruption of the war could readily explain a number of the omissions, others cannot be so reasonably condoned. To cite a single instance, a discussion of gaseous metabolism without reference to Benedict or duBois must fall short of a complete exposition of the topic. Of the author's own prolificity, frequent quotation leaves no doubt. Particularly is he indebted to his earlier publication on "The Significance of Catalysis for Medicine."

Certain earlier generalizations which have lost a portion of their original significance in the light of later experience are apparently regarded as still to be designated as laws ("gesetze").

In the somewhat frequent application of this term to generalizations of varying degrees of validity one is inevitably reminded of the Dooley saying of two decades ago concerning "buildings called sky scrapers—but not by the sky."

A third portion of the book is devoted to a description of the technical details of certain physical chemical methods which have been applied to diagnostic procedures. Many of the illustrations are familiar to those who have had occasion to consult the catalogs of several well-known purveyors of apparatus.

To summarize briefly: the book shows evidence of the expenditure of much labor. There is, however, a distinct lack of critical evaluation of much included material. With the several excellent treatises in this field from authors evidencing a more catholic taste in current literature there does not seem to be a searching need for the present volume.

The make-up of the book reflects the material difficulties with which Germany is now contending.

A. W. Rowe

Die Physikalische Chemie in der Inneren Medizin. Die Anwendung und die Bedeutung Physikochemischer Forschung in der Pathologie und Therapie fur Studierende und Aerzte. (Physical Chemistry as Applied to Internal Medicine. The Application and Significance of Physicochemical Studies in Pathology and Therapeutics. For Students and Physicians.) By Prof. Dr. H. Schade. Thirdd enlarge

and revised edition. Theodor Steinkopff, Dresden and Leipzig, 1923. viii + 605 pp. 120 figs. 24.5×16 cm. Price unbound \$2.80; bound \$3.70.

While the preceding review was in press, a third and revised edition of the work has appeared. Beyond the expansion of certain sections by the inclusion of more recent citations, chiefly local in origin, no significant changes have been made. A number of minor inaccuracies occurring in the first edition remain uncorrected. The insertion of the index to Part I in the body of the book is an innovation of dubious value. The quality of press work and stock is improved but still leaves much to be desired.

A. W. Rowe

Practical Physiological Chemistry. By Philip B. Hawk, M.S., Ph.D., Professor of Physiological Chemistry and Toxicology in the Jefferson Medical College of Philadelphia. Eighth edition, revised. P. Blakiston's Son and Co., Philadelphia, U. S. A., 1923. xvi + 693 pp., 6 full page color plates and 197 figs. Price \$5.00.

Since the first appearance of this work in 1907, it has passed through a number of editions until in 1923, the 8th revision appears. Originally intended as a laboratory manual, it has grown steadily until it is now a somewhat compendious compilation of laboratory methods. This growth, while it has enriched the volume as a work of reference has, in large measure, nullified the original purpose. A patent cause of the embarrassment of riches is the attempt to unite in one volume the materials for a course in biochemistry suitable for collegiate instruction, with those of a diagnostic technical character designed for the instruction of medical students. The chapters on "Gastric Analysis" and "Respiration and Acidosis" are eminently cases in the latter point. This enlarges the book far beyond any practical compass as a teaching manual, and entails a repetition of early experiments under later captions.

In the chapter on "Metabolism" it is a little difficult to understand the inclusion of 20 pages of animal experimentation, although the lucidity of the text and the attractiveness of the illustrations make it both interesting and stimulating. It is to be regretted also that in the selection of analytical methods the author does not exercise a larger measure of critical scrutiny, thereby lessening the somewhat bewildering multiplicity of procedures for the determination of a single substance. To summarize, in its present form the book occupies that debatable middle ground between the real laboratory manual designed for the conduct of a specific course, and the encyclopedic compendia of laboratory methods such as so frequently appear under the editorship of the prolific Abderhalden.

On the other hand, the book possesses many admirable qualities. The introductory paragraphs of each chapter are most judicious summaries of the facts and theories to illustrate which the experiments are designed. The author enjoys a most happy faculty of presenting his matter with clarity, simplicity and accuracy. These qualities, applied as they are to

the individual directions for experiment, offer the maximum of assistance to the student, while in no sense restricting individual performance. The illustrations are numerous and admirably chosen. The summaries in systematic form cannot fail to appeal to teacher and student alike. The appendix, repeating the directions for preparation of reagents and solutions, originally presented as footnotes, is an excellent feature. The index is complete and well arranged.

If the author could be persuaded to divide his material into two volumes, thus conserving the needs of his dual public, the objections to the present text would be in large measure eliminated. And teachers and students in the several fields of pure and applied biochemistry would be greatly enriched thereby.

From the publisher's standpoint the book is handsomely and durably fashioned. Freedom from typographical error is an added attraction.

A. W. Rowe

The Chemistry of Tuberculosis. By H. Gideon Wells, M.D., Lydia M. DeWitt, M.D., and Esmond R. Long, Ph.D., Professors in the University of Chicago and in Rush Medical College. Williams and Wilkins Company, Baltimore, U. S. A., 1923. vii + 447 pp. 7 figs. 23.5 × 15.5 cm. Price \$5.00, United States; \$5.25, Canada; \$5.50 other countries; net, postpaid.

This volume is the outgrowth of the bibliographical phase of the studies on tuberculosis carried out at the Otho S. A. Sprague Memorial Institute. The authors state in the preface that it supplements the earlier monograph by Ott published in 1903. They could with full justice have claimed that, in large measure, it replaces it. The majority of citations are from the literature of the last two decades, during which time refinement and development of chemical methods have rendered obsolete much of the carefully compiled but regrettably erroneous data of the earlier period. The application of physicochemical concepts and generalizations to the problems of biology has also wrought changes of far reaching import and significance. In the present volume, while the cited literature is by nomeans exhaustive, this is evidently the result of a nice discrimination. Particularly to be commended is the just and balanced use of the authors' own material.

Pertinent and significant reference is naturally made, but there is wholly lacking that textual absorption that is an unfortunate and limiting feature of certain similar publications. Recognizing the existence of two schools of practice, it may be suggested that the uniform inclusion of the author's name with the literature citation would be an improvement. Further advantage might be secured by an alphabetical arrangement of all citations in an appendix.

The book is divided into unequal thirds, each dealing with a special phase of the topic. The introductory chapters on the chemistry of the

acid fast bacteria are written by Dr. E. R. Long. The chemical composition of the bacillus and its various metabolic activities are fully treated, and a special chapter is devoted to the property of acid fastness. The second section, which comprises approximately half of the volume and deals with a discussion of the chemical changes in the host, is from the pen of the senior author. Readers who have enjoyed the succinct and graphic summaries in the author's "Chemical Pathology" will derive equal pleasure from the present volume. Restatement of citations is here and there observed, but a fresh connotation usually warrants the repetition.

The inclusion of brief but lucid comparisons and contrasts with pathological states other than that of the thesis adds to the value of the book to the general scientific reader, and attests quietly and convincingly the author's breadth of perspective.

The concluding chapters of the book, written by Dr. L. M. DeWitt, deal with the chemotherapy of tuberculosis. As is implied in the character of research to which the Sprague Institute is dedicated, citation from local sources is here more frequent. With its intrinsic connection with the problem in hand, however, it but emphasizes the scope and value of the studies which have there found their genesis.

All in all, the authors have rendered a very real and definite service to the scientific public, for while the individual worker must go to his original sources, the summary here critically presented, should make unnecessary many hours of fruitless labor.

Mechanically, the press work is excellent, and there is an almost complete absence of typographical error. The probable appearance of a new edition in the near future will, it is hoped, offer opportunity for the use of a more substantial binding.

A. W. ROWE

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THE SOLUBILITY AND SURFACE ENERGY OF CALCIUM SULFATE

By Merle I. Dundon¹ and Edward Mack, Jr. Received April 9, 1923

It is well known in a qualitative way that the solubility of very fine particles is greater than that of coarse ones. This is exemplified in the ordinary custom of digesting precipitates in order to facilitate their filtration. The importance of having available some quantitative knowledge of just how solubility depends on size is very apparent. Such data are needed in elucidation of the surface-energy relations of solids such as are now involved in the study of the colloidal state. In spite of its importance, however, the only available experimental data in this field are those of Hulett² for calcium and barium sulfates, and for mercuric oxide, and even these are admittedly qualitative.

In the present paper and the one which follows,^{2a} we have repeated some of Hulett's work and have extended his general experimental method to several other substances in an effort to obtain reliable values for their surface energy.

- ¹ Grasselli Fellow, 1921-1922.
- ² Hulett, Z. physik. Chem., 37, 385 (1901); 47, 357 (1904). It is true that Marian Jones and J. R. Partington [J. Chem. Soc., 107, 1019 (1915)] measured the increased solubility of small calcium sulfate particles. Sauer [Z. physik. Chem., 47, 160 (1904)] also mentions incidentally the increased solubility of finely pulverized calomel in connection with the use of a calomel electrode. But it is not reported in either of these papers that the size of the particles was measured. It should be noted also that F. C. Thompson [Trans. Faraday Soc., 17, 391 (1922)] by quenching an iron-carbon alloy at 780°, then tempering part of it at 500° and another part at 650°, obtained cementite grains of different sizes. He determined the concentration of the carbon dissolved in the iron in the two cases by measuring the electrical resistance, and calculated an interfacial tension of 1350 dynes/cm.
 - ^{2a} Dundon, This Journal, 45, 2658 (1923).

Theoretical Part

Surface energy, σ , has been calculated by Hulett and by Freundlich, by substitution in the Ostwald-Freundlich equation,³

$$\frac{RT}{M} \ln \frac{S_2}{S_1} = \frac{2\sigma}{\rho} \left(\frac{1}{r_2} - \frac{1}{r_1} \right)$$
 (1)

where R is the gas constant, T the absolute temperature, M the molecular weight of the solid in solution, ρ the density of the solid, σ the surface energy per unit surface between the solid and its solution, and S_2 and S_1 are the solubilities of the particles of radii r_2 and r_1 , respectively. In the derivation of this equation it is assumed that the particles are spherical, that the dissolved solid obeys the gas laws, and that σ and ρ are independent of the size of the particles. Equation 1 does not hold for dissociated substances. Jones takes into account the dissociation of the dissolved substance by combining Equation 1 with the equation of Storch, which is

$$\frac{(1-\alpha)}{v} = K\left(\frac{\alpha}{v}\right)^m \tag{2}$$

where α is the degree of dissociation, v is the dilution and K and m are constants. When m is 2, Storch's equation becomes the familiar Ostwald dilution equation. The equation which Jones derived, by a combination of Equations 1 and 2 and by integrating between the limits α_1 and α_2 , is

$$\frac{2\sigma}{\rho} \left(\frac{1}{r_2} - \frac{1}{r_1} \right) = \frac{RT}{M} \left[(n-1) (\alpha_1 - \alpha_2) - \frac{n}{m-1} \ln \frac{1 - \alpha_1}{1 - \alpha_2} + \frac{m}{m-1} \ln \frac{\alpha_1}{\alpha_2} \right]$$
(3)

where n is the number of ions formed from the dissociation of one molecule. While this equation is theoretically sound, its practical application is complicated by the fact that concentrations are expressed only in terms of dissociation and the constant m in Storch's equation. Inasmuch as small differences in dissociation correspond to rather large changes of concentration, small errors in expressing dissociations are quite serious.

In these fundamental derivations the ordinary expression for osmotic work done is $\frac{RT}{M} \ln \frac{p_2}{p_1}$ for one mole of dissolved solute. Then, if a substance is dissociated and we assume that this dissociation is constant during the process, Equation 1 becomes

$$(1-\alpha+n\alpha)\frac{RT}{M}\ln\frac{S_2}{S_1}=\frac{2\sigma}{\rho}\left(\frac{1}{r_2}-\frac{1}{r_1}\right) \tag{4}$$

³ First derived in its most general form by Willard Gibbs in 1876, "Scientific Papers," Longmans, Green and Co., 1906, N. Y., vol. I, p. 315.

⁴ William Jacob Jones [Ann. Physik, 41, 441 (1913)] has considered the influence of various geometrical forms instead of the spherical particles assumed in the general equation.

⁵ W. J. Jones, Z. physik. Chem., 82, 448 (1913).

⁶ Storch, ibid., 19, 13 (1896).

Values obtained by this simple equation approximate closely to those calculated by means of the rigorous equation of Jones, the differences being very small in comparison with the errors inherent in the data.

There is another point in this connection which is important. In substituting numerical values for the radii in the expression $\frac{2\sigma}{\rho}\left(\frac{1}{r_2}-\frac{1}{r_1}\right)$, r_2 is the radius of the smaller and more soluble particles, and is, of course, measured by microscopic observation; r_1 represents the radius of a large particle, in equilibrium with its own saturated solution. In Hulett's work (and also in the present work) this saturated solution containing the large particles was simply a saturated solution of the substance in equilibrium with large crystals. Since the crystal surfaces were flat, $1/r_1$ is $1/\infty$. It is true that Hulett's results seemed to show that particles 2μ in diameter were also in equilibrium with the saturated solution of the crystals. But one cannot be absolutely certain of the equilibrium, and if it is a question of choosing between $1/\infty$ and $1/2\mu$ there can be no doubt that it is preferable to write $1/\infty$ into the equation. In this case, Equation 4 assumes the form

$$(1 - \alpha + n\alpha) \frac{RT}{M} \ln \frac{Sr}{S} = \frac{2\sigma}{\rho r}$$
 (5)

and this is the equation which we have used throughout our work in calculating the surface energy.

In an interesting paper, Marian Jones and J. R. Partington have attempted to test the validity of Equation 1 at 20°, 40° and 60°. Taking the known concentrations of saturated calcium sulfate solutions in equilibrium with gypsum crystals, they substitute these values for S_1 in Equation 1 and calculate S_2 for the respective temperatures and for various values of r_2 , setting $r_1 = \infty$, and making use of W. J. Jones' surface-energy value, 1050, calculated from Hulett's data. They have not measured the size of their particles, but have assumed a radius of 1μ , because their experimentally determined solubilities fit their calculated solubility curve for particles of this size. The surface-energy value, 1050, which takes into account the dissociation of the calcium sulfate, has unfortunately been substituted in Equation 1, which does not hold for dissociated substances. The result is that all of their calculated solubilities and radius values are much too high. This error is evident from the fact that their fine particles which give an increased concentration of 4.6% at 20° are considered to be of the same size as were found by Hulett to show no increased solubility, although their own calculations are based on Hulett's data.8

⁷ Jones and Partington, J. Chem. Soc., 107, 1019 (1915).

⁸ It has seemed desirable to call attention to the difficulties with the conclusions reached by Jones and Partington, because the substance of their work has already been incorporated into two well-known chemical texts.

Experimental Part

The method we have employed in measuring the increased solubility of small particles of calcium sulfate is essentially the same as that of Hulett. Into a saturated solution of calcium sulfate in equilibrium at 25° with large crystals, a quantity of the finely powdered calcium sulfate was introduced. The increase in concentration, and the return to the original concentration were noted by conductivity measurements. In order to calculate the concentration of a solution of a dissociated substance from the conductivity by means of the formula, $\frac{\text{millimoles}}{\text{liter}} = \frac{k}{2\alpha\Lambda_{\infty}}$, it is necessary to know the degree of dissociation α . For strong electrolytes Storch's dilution law holds and can be applied to supersaturated solutions. That equation, however, contains two unknowns and cannot be solved for α , but corresponding values for concentration (1/v) and dissociation (α) may be determined by the method of trial and error. this way values of 1/v and α corresponding to the conductivity of the solution in question are found. A at 25° was taken as 126. Concentrations of calcium sulfate can also be calculated from the conductivity value at 25° by the empirical formula of Hulett, $\frac{\text{millimoles}}{\text{liter}} = -0.354 +$ $5211 (k_{25}) + 841400 (k_{25})^2$.

Calculations to millimoles per liter for two supersaturated solutions gave by the first method 15.59 and 48.84, and by Hulett's equation 15.54 and 49.35, respectively. In view of the evident agreement the simpler formula of Hulett was used in all subsequent calculations, for even though absolute values might be slightly different the percentage increase would be the same.

Preparation of the Salt.—Large crystals of calcium sulfate were prepared by allowing solutions of calcium chloride and of sulfuric acid to drop slowly into 3 liters of hot, well-stirred, distilled water. The precipitate was then thoroughly washed eight times, using 2 to 3 liters of distilled water each time. In this way a pure sample of crystals $20-50\mu$ long was obtained. Analysis showed that its water content was 21.1%. A second analysis checked exactly with the first. The theoretical water content of the dihydrate, CaSO₄. $2H_2O_7$, is 20.93%.

The Kohlrausch type of conductivity cell with platinized electrodes that was used could be shaken violently by hand immediately upon addition of the powder.

Experiment 1.—Some of these large crystals were ground by hand in an agate mortar to a fairly uniform average size of 0.3μ . Part of this powder (0.4 g.) was added to about 40 cc. of the saturated solution in a conductivity cell and in one minute the conductivity rose from the original value of 2208×10^{-6} to 2616×10^{-6} . After two days it had returned

⁹ Hulett, Z. physik. Chem., 42, 581 (1903).

to 2276, and after six days to 2213 \times 10⁻⁶. The only large crystals, with which the final solution was presumably in equilibrium, were those large fragments introduced along with the fine powder. When calculated to concentration values, the increase was about 24%.

Analysis of a portion of the powder which had been ground in the agate mortar, showed that its water content was only 12%. Evidently, the grinding treatment had partially dehydrated it. This effect has been observed by Sullivan and Steiger, 10 who reduced the water in gypsum to about 5% by long grinding. Since it is well known 11 that dehydrated calcium sulfate is much more soluble than the dihydrate, it may be true that part, at least, of the observed increase in solubility noted in this experiment may have been due to the presence of the dehydrated material. Hulett, in fact, was careful to call attention to such a possibility. Practically the same result that has been noted in this experiment with precipitated calcium sulfate, has also been found with natural gypsum. With ground gypsum particles 0.3μ in diameter and a water content of 15%, an increase in concentration of 28% was observed.

Experiment 2.—The greater solubility of the dehydrated material may be shown in a very striking way. When calcium sulfate which has lost a few per cent. of its water content is added to a drop of water under the microscope, long needle-like crystals of the dihydrate form rapidly, thus showing a high degree of supersaturation. But the needles do not form if the added powder contains its full amount of water of crystallization, even though it be very finely divided.

Experiment 3.—To the same saturated solution in equilibrium with the large crystals used in Expt. 1, were added some of these same large crystals which had been dehydrated by heating. The crystals were not ground. The conductivity moved from the original value of 2208×10^{-6} to 2450×10^{-6} in one day, and in two days to 2520×10^{-6} . When filtered and seeded with the original hydrated crystals, the conductivity returned after four days to practically its original value. The question at once arose as to whether or not heating the crystals resulted in pulverization by decrepitation. Microscopic examination of the dry crystals failed to show the presence of fine particles, and the very slow rate of increase of the conductivity also indicated that small particles were not present.

This experiment shows that it is possible to increase the concentration without powdering the calcium sulfate, if it is dehydrated. It is interesting to note, incidentally, what happens to the dry crystals which have been dehydrated, when a drop of water is added to them on a microscopic slide.

¹⁰ This observation is given by W. F. Hillebrand, This Journal, 30, 1120 (1908).
Compare John Johnston, Rec. trav. chim., 42, 850 (1923).

¹¹ Marignac, Ann. chim. phys., (5) I, 274 (1874). Cavazzi, Industria chimica, 1906, 366 (1906).

They are at once broken up into much smaller crystals, as though the water violently works its way with a disruptive force into porous places which have been produced in the crystals by the heat treatment.

Experiment 4.—It is evidently not at all an easy matter to grind calcium sulfate crystals without causing partial dehydration. An attempt was made to do this by grinding the precipitated crystals between two glass plates wetted with petroleum ether. The powder analyzed 21.1% water. Most of it was about 0.5μ in diameter, with very little smaller than that. The increase in concentration obtained was 4.8%.

The crystals can be ground between glass plates without the addition of petroleum ether and the powder will show by analysis its full water content, but it is difficult to obtain powder even as small as 0.5μ , because of the stickiness and the great resistance to rubbing.

Experiment 5.—In a further attempt to prevent dehydration on grinding, some clean natural gypsum crystals were ground in an agate mortar in a small room where the air was kept saturated by vapor from boiling water. The temperature was about 25°. Each lot of 0.1 g. powder was ground for 20 minutes. The powder so prepared showed a water content of 18.5%. It was then taken in small lots in the mortar, wet with conductivity water, ground until dry, and the resulting lumps were powdered. Analysis gave 21.0% water. Most of the particles were about 0.5μ in diameter, with a few 0.4μ . An increase in concentration of 4% was found.

Experiment 6.—It was observed, during examination of fine calcium sulfate particles under the microscope, that if water was used to wet the particles, a slight rubbing with the glass cover slip seemed to break them up into much smaller pieces. This suggested that the substance might be ground satisfactorily in the presence of water. Therefore, precipitated calcium sulfate crystals were wet with conductivity water and ground by hand in an agate mortar until dry. The resulting dry lumps were then ground until thoroughly powdered. The water content was 21.3%. The powder grains appeared very irregular in shape, and a large percentage of them were about 0.2μ , and some 0.3μ in diameter. The increase in concentration, as shown by conductivity measurements, was 12.3%.

Experiment 7.—Some of the ground powder used in Expt. 4, showing a water content of 21%, was heated at 100° for half an hour, until its water content had dropped to 15.5%. This powder when added to the saturated solution in the conductivity cell, showed an increase of 257% in concentration. There did not seem to be many smaller particles present after the heating than before, although, of course, there may have been a great deal of material too small to be visible in the microscope.

Discussion of Results

Examination of the results in Expts. 4, 5 and 6, shows that where precautions were taken to avoid dehydration, the increase in solubility due to the small size of the particles was not very great. In Expts. 4 and 5, where particles about 0.5μ in diameter were used, the average surface energy, calculated from Equation 5, taking i (that is, $1-\alpha+n\alpha$) as 1.56, was 356 ergs per sq. cm. Calculation by Jones' Equation 3 gave 352 (a difference of about 1%), while an error of only 0.01μ in the diameter measurement would make a difference of 2% in the value for surface energy. In the microscopic estimation of the size of particles, the probable error is much greater than 0.01μ . It is more nearly 0.1μ . Thus it is clear that the simplified Equation 5 is amply sufficient for present needs. It is also clear that very little reliance should be placed on our present knowledge of the surface energy of solids.

In Expt. 6, where the particles were estimated at 0.2μ in diameter, the calculated value of the surface energy was 385. The average for the two sizes, 0.5 and 0.2μ , is then about 370.

The question now arises as to why the above result differs from that of Hulett, who found a much larger increase in solubility. The possibility of slight dehydration is suggested by the fact that he does not specifically mention any moisture determination on his fine powder. Moreover, gypsum crystals are transparent, and have a low refractive index, and when finely powdered are difficult to observe sharply in the microscope, so that it is very uncertain how many particles too small to be visible might be present in the powder. When the material was wet almost until the last stage of grinding, as in our own Expts. 5 and 6, the probability of the occurrence of invisible small particles would be greatly lessened.

We wish to express our gratitude to the Grasselli Chemical Company for the fellowship grant under which this investigation was carried on.

Summary

- 1. A brief discussion is given of errors which appear in the literature in the calculation of surface energy and size of particles of calcium sulfate based on Hulett's data.
- 2. On the basis of the simplifying assumption that the degree of dissociation does not change with small changes of concentration, the van't Hoff factor, i, is introduced into the Ostwald-Freundlich equation, to replace the complicated correction formula of W. J. Jones.
- 3. Experimental data have been produced which show the great tendency of gypsum and precipitated calcium sulfate, CaSO₄.2H₂O, to become dehydrated during grinding, and the importance of this factor in relation to experiments on the solubility of finely powdered calcium sulfate.
- 4. Working with particles 0.2μ and 0.5μ in diameter a value of about 370 ergs/sq. cm. has been calculated for the surface energy of the dihydrate of calcium sulfate.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

THE PHOTOGRAPHIC SENSITIVENESS OF SILVER IODIDE

By Frank E. E. Germann and Malcolm C. Hylan¹

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Introduction

It has long been known that photographic emulsions containing silver iodide appear to be much less sensitive than do silver bromide emulsions. Should we expect this from purely theoretical considerations?

The photographic process may be roughly divided into two parts, (a) the photochemical effect of light upon the plate, and (b) rendering this effect visible by the process of development. It is with the first of these that we are concerned. There are at present several theories as to the exact nature of the action of light upon the plate, of which probably the most acceptable are the "nuclear" theory and the "sub-halide" theory.

Luther² claims that when a pure silver halide is exposed to light it undergoes reduclight

tion according to the equation, $2AgX \longrightarrow Ag_2X + X$. When the light is removed the dark sub-halide recombines with the free halogen according to the equation, $AgX + X \longrightarrow 2AgX$. Trivelli³ represents the photochemical action by a series of steps, with the formation of several sub-halides; in each step halogen is liberated. The original and final stages may be represented as follows, $Ag_nX_n \Longrightarrow nAg + \frac{n}{2}X_2$.

Lüppo-Cramer⁴ is an exponent of the nuclear theory which according to Lorenz⁵ may be expressed approximately by the equation, $nAgX + light \longrightarrow (n-1)AgX + Ag + X$. The silver particles liberated act as nuclei for the condensation of more silver during development.

It is to be noted that by each of these theories halogen is liberated, and from the law of mass action the reaction should proceed with greater velocity and more nearly to completion if this halogen were removed. So to represent the reaction more accurately, the equation (taking only the

first one given above) should be written, $2AgX + gelatin \longrightarrow Ag_2X + halogenated gelatin.$

The relative sensitivity of silver bromide and silver iodide must depend, in part at least, upon the speeds of their corresponding reactions. From the above equation we can see two factors which affect the speed of the reaction. The first of these is the stability of the silver halide. It is well known that bromine is more active than iodine, and has a greater affinity

- ¹ Extract from a thesis submitted by Malcolm C. Hylan in partial fulfilment of the requirements for the degree of Doctor of Philosophy.
 - ¹ Luther, Z. physik. Chem., 30, 628 (1899).
 - ³ Trivelli, Jahrb. Radioakt. Elektronik, 8, 334 (1911).
 - Lüppo-Cramer, "Kolloidchemie und Photographie," Steinkopf, 1921.
 - ⁵ Lorenz, Z. Elektrochem., 7, 277 (1900-1901).

for metals. This is evidenced by the fact that bromine will displace iodine from its salts. Silver and bromine, then, in silver bromide should be more strongly bound together than silver and iodine in silver iodide. Conversely, silver iodide should be more easily broken down by the action of light. This factor would seem to favor the greater speed or sensitiveness of silver iodide.

The second factor is the combining power of halogen and gelatin. Here, bromine, being the more active, would be expected to combine more readily. We shall show later that this is actually the case. This factor would seem to favor the greater speed of silver bromide. We have, then, our two factors opposed, and the relative speeds of bromide and iodide must depend, in part, upon the relative magnitudes of the two factors. Other factors, as we shall show, may also enter to affect the relative speeds of the two reactions.

J. A. Johnson⁶ has recently discovered a method for making iodide emulsions as sensitive as bromide emulsions. His patent is described as follows.

"For the production of high-speed print-out papers, plates, films, etc., coated with a light sensitive silver iodide emulsion. The emulsion may be produced by treating paper coated with silver chloride, bromide, or bromo-chloride emulsions with a soluble iodide, or by coating the paper directly with a gelatin or collodion emulsion, and sensitizing the emulsion after drying with a solution containing an organic sensitizer such as 'monomethylparaamidophenol sulfate' and an inorganic accelerator such as sodium sulfite. The sensitizing operation may be performed in daylight, since the sensitized emulsion does not become light sensitive until it is dried. The visible image produced on printing may be fixed by merely washing in water to remove the sensitizer; the unchanged silver iodide remains in the emulsion but is light insensitive."

The details of the above were communicated to the former of us before the patents were issued, and the desire was expressed that the theoretical side might be investigated. A careful study of the process should disclose the true causes of the lack of sensitiveness of ordinary silver iodide, and in what manner they may be overcome.

Experimental Part

Relative Combining Power of Bromine and Iodine with Gelatin.— Experiments to determine the relative combining power of bromine and iodine with gelatin were performed as follows.

A solution of iodine in potassium iodide was titrated against sodium thiosulfate solution. Five cc. of iodine solution was found to be equivalent to 2.4 cc. of thiosulfate solution. A concentrated solution of potassium iodide was then prepared and bromine water was run in, liberating iodine according to the reaction $Br + KI \longrightarrow KBr + I$. The liberated iodine was titrated against sodium thiosulfate. In this way 5 cc. of bromine was found to be equivalent to 3 cc. of thiosulfate solution, or 4 cc. of the bromine solution was equivalent to 5 cc. of the iodine solution. About 4 g. of gelatin was dis-

⁶ Johnson, C. A., 16, 3270 (1922).

solved in 150 cc. of distilled water and divided into 4 equal parts. To each of two of these 8 cc. of the bromine solution was added; to each of the other two 10 cc. of iodine solution was added. To each of the gelatin-bromine solutions was added as much crystalline potassium iodide as a spatula blade would hold and the liberated iodine was titrated with thiosulfate. In both cases only 0.3 cc. of the thiosulfate was required, indicating that about 95% of the bromine had combined with the gelatin. Two gelatiniodine solutions were then titrated with thiosulfate. In each case 5 cc. was required, indicating that practically none of the iodine had combined with the gelatin.

Experiments on Silver Iodide Emulsions.—Silver iodide emulsions were experimented upon directly in order to study their photosensitive characteristics and to determine the role played by Johnson's sensitizer. Excess of potassium iodide gave an emulsion that was not affected by light, was non-sensitive without treatment but was sensitized by bathing in Metol-sulfite solution, was not affected by light before sensitization and was accelerated by bathing in silver nitrate. Excess of silver nitrate, on the other hand, gave an emulsion that darkened on exposure to light, was sensitive without treatment, was unaffected by the Metol-sulfite solution, blackened when sensitized if previously exposed to light and was retarded by bathing in potassium iodide solution.

Johnson's emulsions contain an excess of potassium iodide. When they are washed for an hour in cold water an emulsion containing a large excess of potassium iodide is, after sensitizing, as fast as one containing much less potassium iodide, but when not so washed the greater the excess of potassium iodide the slower the paper. Furthermore, in this connection, small amounts of potassium iodide present in the developer bath act as very strong retarders or, if in sufficient amount, stop all action. It is well known that potassium bromide has a similar action in the development of bromide papers, although to a less degree.

Sensitizing Effect of Various Chemicals.—The effect of sensitizing with various developers was tried and a solution of monomethyl-p-amidophenol sulfate (Metol) with sodium sulfate was found to be the best. The sensitizing effect of several inorganic compounds was tried, a summary of which is given in Table I.

		TABLE I	
	SENSITIZING	Effect of Chemical Substance	\$S
Sensitized with	Exposure	Treatment	Results
Dil. H ₂ S	5-20 sec.	∫ Bathed in Metol, then in \	Water tenance
Dil. Na ₂ S ₂ O ₃	5–20 sec.	dil. alkaline Na₂SO₃ ∫	Fair image
$5\% \text{ Na}_2\text{S}_2\text{O}_3$	1 min.	Dil. alkaline Na ₂ SO ₃	
Dil. NaOH	5-15 min.	Bathed in Metol	
Dil. KOH	3-5 min.	Bathed in Metol	Faint image
5% Na ₂ SO ₃	3–5 min.	Metol, then alkaline sulfite	
5% NaHSO ₃	3-5 min.	Metol, then alkaline sulfite	
0 % Namous	5-5 mm.	Metol, then alkaline suinte	es .

Attention should be called to the fact that by sensitizing with 5% thiosulfate an image was obtained although no organic developer had been used at any stage of the process.

Properties of a "Neutral" Emulsion.—An emulsion having, within the limits of experimental error, no excess of either potassium iodide or silver nitrate was prepared as follows.

Ten g. of potassium iodide was dissolved in 100 cc. of distilled water (designated as Solution A). Ten g. of silver nitrate was dissolved in 40 cc. of distilled water and ammonium hydroxide added until the precipitate, at first formed, redissolved (designated as Solution B). Twenty-five cc. of Solution A was placed in a conductivity cell and the opposing resistance adjusted to give a reading near the center of the bridge. Solution B was added, 1 cc. at a time, the bridge reading being taken after each addition, until 20 cc. had been added. The experiment was then repeated, using 15 cc. of Solution A and adding 15 cc. of Solution B. Graphs were then made by plotting bridge readings against cc. added, and the volume of B corresponding to the break in the curve was determined. For the first titration 16.2 cc. of Solution B was equivalent to 25 cc. of Solution A. For the second titration 15.8 cc. of Solution B was equivalent to 25 cc. of Solution A. The average of the two is 16 cc.

From a buret, then, exactly 25 cc. of Solution A was run into a beaker, 5 g. of gelatin added, and the whole warmed until the gelatin had dissolved. Then exactly 16 cc. of Solution B was added.

The emulsion thus formed was painted on cards and dried. After about 4 hours, the cards, feeling dry to the touch, were exposed for 6 seconds, and bathed first in Metol, then in alkaline sulfite solution. A very good image was obtained.

Effect of Moisture.—Two or three days later some of these same cards were exposed and developed and the image found to be very much fainter than before. As the only difference between the cards at the two different times could be the amount of moisture in the emulsion, some of the cards were soaked in water for a minute and dried until they felt dry to the touch. Upon exposing and developing them very good images were again obtained.

To avoid the double bathing necessitated, in the case of iodide emulsions, by the use of the alkaline sulfite bath following bathing in the ordinary Metol developer, a developer was prepared by adding about 1% of sodium hydroxide to the Metol-sulfite solution, and was found to work well. Some of the cards covered with iodide emulsion, prepared according to Johnson, that is, with excess of potassium iodide, which had been coated several weeks previously, were exposed for 6 seconds and bathed for 10 minutes in this developer. A faint image was obtained. An iodide card covered with iodide emulsion prepared by converting a card covered with bromide emulsion, when exposed 6 seconds gave no image, even after 45 minutes' bathing in the developer. A "prepared" iodide card and a "converted" iodide card were then soaked in water for a minute and, after drying, exposed, the former for 6 seconds, the latter for 24 seconds. The former on 10 minutes' bathing in the developer gave a clear but light image: the latter, after 15 minutes' bathing, showed a faint trace of an image. The great difference between the "prepared" and "converted" cards is probably due to the fact that the latter have a surface coating of gelatin over the emulsion, put on to prevent abrasions, and to obtain results it is necessary to work down through this.

To compare the effect of moisture on bromide emulsions, a card covered with bromide emulsion was cut in two, and half soaked in water for a minute and dried. Both halves were then exposed for one second and bathed in developer for 15 seconds. At the end of that time the moistened card bore a good image, but the unmoistened card was still blank.

Comparison of Accelerating and Retarding Effects.—Three cards from the carefully prepared "neutral" emulsion, that is, having no excess of either potassium iodide or silver nitrate, were treated as follows. One was soaked in clear water, one in dil. potassium iodide solution, and one in dilute thiosulfate solution. After drying, each was exposed for 6 seconds and bathed in the alkaline developer for 15 minutes. The card treated with thiosulfate gave a very good image, the water-treated card a medium one, and the potassium iodide-treated card a poor one.

Discussion

The evidence of our experiments indicates that it is principally adsorbed potassium iodide which causes the apparent non-sensitiveness of silver iodide emulsions. That potassium iodide is adsorbed by silver iodide has been shown by Lottermosser and Rothe.⁷ Theoretically, we should not expect potassium iodide to have any greater retarding effect on silver iodide than potassium bromide on silver bromide. The fact that its retarding action is much greater can be easily explained on the basis of adsorption. To quote Lüppo-Cramer,⁸ "silver iodide in general possesses a higher degree of dispersity than the other silver halides." Consequently, a given weight of silver iodide has a much greater specific surface than the same weight of other silver halides, and therefore is capable of adsorbing much more soluble halide.

The experimental evidence in support of the above hypothesis may be briefly summarized as follows, remembering that when emulsions are spoken of as sensitive and non-sensitive we refer to the ability to produce an image after exposures of, at most, but few minutes duration, followed by bathing in the common photographic developers. (1) Emulsions containing no excess of potassium iodide are sensitive. (2) Emulsions containing any excess of potassium iodide are non-sensitive. (3) Considerable washing of an emulsion containing an excess of potassium iodide will not render it sensitive. (4) The presence of mere traces of potassium iodide in the developer bath retards or, if in sufficient amount, stops all action. (5) Bathing the emulsion in dilute solutions of compounds which

⁷ Lottermosser and Rothe, Z. physik. Chem., 62, 377 (1908).

⁸ Lüppo-Cramer, Kolloid Z., 30, 186 (1922).

would react with any adsorbed potassium iodide, thus removing it, renders the non-sensitive emulsion sensitive. This last point might easily be taken as due to the presence, in the emulsion, of reagents that combine with the liberated iodine. However, as they should react metathetically with any potassium iodide present long before exposure, it is likely that they function in both ways. In support of our hypothesis, and in harmony with (3) above, let us quote Trivelli and Sheppard⁹—"the separation (of adsorbed contaminants) by washing with pure solvent proceeds very slowly, adsorption being in most cases practically irreversible."

Our views find further confirmation in the work of Lüppo-Cramer¹⁰ who found that a partial transformation of silver bromide or silver chloride into silver iodide is associated with a great increase in sensitivity, but that a complete transformation into silver iodide results in a marked decrease in sensitivity. He says, in explaining this fact, "It seems probable that in the case of a complete transformation, the hard-to-be-avoided excess of soluble iodide, which is held stubbornly adsorbed by the silver iodide, is the cause of the reversal of sensitiveness."

Renwick,¹¹ too, attributes the loss in sensitivity on converting bromide plates into iodide, in part "to the great capacity of silver iodide for adsorbing soluble iodides, which would very much increase the difficulty of reducing it to metallic silver by alkaline development."

In the light of our hypothesis we can easily explain why, with the washed emulsions, it makes no difference how much potassium iodide is in excess, while with the unwashed emulsions the excess of potassium iodide is measured by the retardation of development. In the first case the free or unadsorbed potassium iodide is washed out and only the adsorbed remains, while in the latter case both adsorbed and unadsorbed potassium iodide are present, and there is, therefore, much more chance that some will be left in to retard development.

Another cause of the apparent non-sensitiveness of ordinary silver iodide emulsions is the absence of a sensitizer, gelatin not combining with iodine sufficiently to play that role. The experimental evidence supporting this conclusion is (1) iodine has practically no power for combining with gelatin; (2) sensitization is effected by addition of hydrogen sulfide, sodium thiosulfate, various sulfites, potassium hydroxide and sodium hydroxide to ordinary iodide emulsions, and is increased by their addition to "neutral" emulsions. Each of these compounds has the power of combining with iodine. The reactions are: $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$; $H_2S + I_2 \longrightarrow 2HI + S$; $3I_2 + 6KOH \longrightarrow 5KI + KIO_3 + 2NaI$; $H_2S + I_3 \longrightarrow 2HI + S$; $3I_2 + 6KOH \longrightarrow 5KI + KIO_3 + 2NaI$

⁹ Trivelli and Sheppard, Eastman Kodak Co., "Monographs on the Theory of Photography," No. 1, p. 30.

¹⁰ Lüppo-Cramer, Phot. Korr., 50, 561 (1913).

¹¹ Renwick, J. Soc. Chem. Ind., 39, 156T (1920).

 $3H_2O.^{12}$ Iodine reacts similarly with sodium hydroxide: $SO_3^+ + H_2O + I_2 \longrightarrow 2H^+ + 2I^+ + SO_4^=.^{13}$

The catalytic effect of moisture is also an important factor in the sensitization of silver iodide emulsions. This probably does not affect the relative speeds of iodide and bromide emulsions, as our experiments indicate that the effect on the one is as great as the effect on the other. However, other factors lower the sensitivity of iodide emulsions to such a degree that it is likely that moisture is an important factor in raising the photochemical action above the "threshold value" of developability.

We conclude then, that silver iodide emulsions are not strictly non-sensitive, but that, quoting Bolas, 14 "whether exposed or unexposed they are almost unaffected by such weak alkaline developers as are used in ordinary photographic practice;" that their low sensitivity is due primarily to the adsorption of potassium iodide, together with its strong retarding effect, and secondarily to the inability of gelatin to act as a sensitizer; and that if a sufficiently strongly alkaline developer is used, in spite of their low sensitivity, fair results may be obtained.

Johnson's process of sensitization does two things: (1) it removes adsorbed potassium iodide, and (2) it leaves organic developer in the emulsion to act as sensitizer, and later as developer. Hence, the emulsion being light sensitive and organic developer being present, all that is necessary to obtain an image is to expose it and then bathe it in dilute alkali to make the developer active. Bathing the sensitized paper in distilled water does not, as Johnson claims, desensitize it. It merely removes the unadsorbed developer dissolved in the emulsion, so that after exposure it is necessary to bathe the paper in organic developer before the alkali bath in order to bring out the image.

Summary

- 1. It is shown that from purely theoretical considerations it is impossible to predict whether or not silver iodide should be photographically more sensitive than silver bromide.
- 2. Johnson's method of sensitizing the apparently non-sensitive silver iodide emulsions is described.
- 3. Experiments have been performed to determine the nature of this process of sensitization.
- 4. It is shown that gelatin, which has a sensitizing effect in bromide emulsions, has practically no sensitizing effect in iodide emulsions.
- 5. Potassium iodide is shown to have a powerful retarding effect, emulsions containing an excess of this reagent being non-sensitive.
 - 6. A number of compounds, both organic and inorganic, which should
 - ¹² Thorpe, Longmans, 1912, vol. III, p. 152.
 - 13 Treadwell and Hall, vol. I, p. 349.
 - ¹⁴ Bolas, Brit. J. Phot., 68, 532 (1921).

react with potassium iodide or with iodine have been shown to have sensitizing effects.

- 7. An emulsion having no excess of silver nitrate or potassium iodide has been prepared and found to be sensitive.
- 8. Washing to remove the excess of potassium iodide does not make the regular iodide emulsion sensitive.
- 9. The amount of moisture present in the emulsion has been shown to have considerable effect on the sensitiveness.
- 10. In general, sensitization has been effected by treatment with a chemical which would react with potassium iodide to remove it, or remain in the emulsion to combine with any iodine liberated.
- 11. The "non-sensitive" emulsions have been found to be sensitive when a strongly alkaline developer was employed.
- 12. It is concluded that the apparent non-sensitiveness of silver iodide emulsions is due primarily to adsorbed potassium iodide, secondarily to the absence of a sensitizer, gelatin not playing that role; and that ordinary, apparently non-sensitive, silver iodide emulsions are truly sensitive when a sufficiently strongly alkaline developer is used.

BOULDER, COLORADO

[Contribution from the Laboratories of General Chemistry of the University of Wisconsin]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY FERRIC SALTS. II

By Van L. Bohnson and A. C. Robertson Received May 21, 1923

It has been known for some time that the decomposition of hydrogen peroxide is accelerated by the presence of iron salts in solution. The most recent quantitative investigations are those which were made by von Bertalan, by Duclaux, by Mummery, and by one of the writers of this paper. The purpose of the present paper is to present the results of subsequent experiments which necessitate certain modifications in the conclusions reached by these investigators. The work already reported was done with very dilute solutions of the catalyzing salts (up to 5 millimoles per liter). More concentrated solutions than this could not conveniently be used by the two first-named writers, owing to the difficulty of following the more rapid reactions by the cumbersome method of titrating samples with permanganate. On the other hand, the gasometric method offers an accurate means of measuring the rate of a reaction so rapid as to be entirely completed in 5 minutes.

¹ von Bertalan, Z. physik. Chem., 95, 328 (1920).

² Duclaux, Bull. soc. chim., 31, 961 (1922).

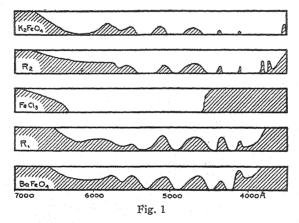
³ Mummery, J. Soc. Chem. Ind., 32, 889 (1913).

⁴ Bohnson, J. Phys. Chem., 25, 19 (1921).

Optical Evidence of an Intermediate Compound

Somewhat indirect evidence led to the suggestion in the previous paper⁴ that ferric acid (H₂FeO₄) is formed by the reaction between hydrogen peroxide and the iron salt, the ferric acid being subsequently reduced with the evolution of oxygen.

This hypothesis has been tested by photographing the absorption spectra of solutions of (1) ferric chloride alone, (2) barium ferrate dissolved in acetic acid, (3) potassium ferrate, and (4) mixtures of hydrogen peroxide and ferric chloride.⁵ The source of illumination and reference was the iron arc; a quartz spectrometer was used, the solutions being contained in a quartz absorption cell. Instead of varying the concentration or thickness of the solution, the times of exposure were increased logarithmically and a number of photographs taken on the same plate in the usual manner. The reaction mixtures were chilled in order to avoid too rapid disappearance of the supposed intermediate compound.



Some of the results are shown graphically in Fig. 1, the shaded portion of which represents the absorption bands, plotted on a uniform scale of wave lengths in Ångstrom units. A striking similarity between the bands for the two ferrates and for the reaction mixtures (R_1 and R_2) is obvious. On the other hand, a solution of ferric chloride of much greater than equivalent concentration shows no such characteristic bands in the yellow and green and is totally opaque to the violet. When hydrogen peroxide is added to the ferric chloride, transmission of violet lines takes place and absorption bands appear in the yellow and green. These results lead to the conclusion that the original hypothesis was correct; namely, that FeO₄ ions are present in the reaction mixture. The difference between R_1 and R_2 in the extreme violet suggests that the former reaction was

⁵ It was suggested by von Bertalan (Ref. 1) that an optical method might indicate the nature of the iron compound present.

nearer completion, there being more ferric chloride present, decreasing the transmission in that region. None of the solutions transmitted wave lengths shorter than 3500.

The Mechanism of the Reaction

It was suggested by von Bertalan that the reaction takes place in the following stages,

$$H_2O_2 + 2 \text{ Fe}^{+++} \longrightarrow 2 \text{ Fe}^{++} + 2 \text{ H}^+ + O_2$$
 (1)

$$H_2O_2 + 2 \text{ Fe}^{++} + 2 \text{ H}^+ \longrightarrow 2 H_2O + 2 \text{ Fe}^{+++}$$
 (2)

the sum of the two yielding the equation for the decomposition of hydrogen peroxide. It is possible to test the probability of these reactions taking place by means of the criterion suggested by Bray,⁶ that each of such a cycle of changes should be accompanied by a diminution of free energy. The standard free energy changes for Reactions 1 and 2 can be calculated, using the following values for the free energy of formation at 25°, in calories, given by Lewis and Randall: 7 H₂O₂ (aq.), -31,470; Fe⁺⁺⁺, -3120; Fe⁺⁺, -20,350; H₂O (1), -56,560; H⁺, 0; O₂ (g), 0.

From these data, ΔF_{298}° for Reaction 1 can be shown to be —2990 cals., while for Reaction 2 it is —47,190 cals. The difference in these values indicates that while ferrous ion may be oxidized to ferric ion by hydrogen peroxide in acid solution, it is not so probable that subsequent reduction will take place.

We have shown experimentally that ferrate ion is formed by the action of hydrogen peroxide on ferric salts. The following must therefore take place,

$$3 \text{ H}_2\text{O}_2 + 2 \text{ Fe}^{+++} + 2 \text{ H}_2\text{O} \longrightarrow 2 \text{ FeO}_4^{--} + 10 \text{ H}^+$$
 (3)

with subsequent reduction of the ferrate ion according to one or both of the following,

$$2 \text{ FeO}_4^{--} + 3 \text{ H}_2\text{O}_2 + 10 \text{ H}^+ \longrightarrow 2 \text{ Fe}^{+++} + 3 \text{ O}_2 + 8 \text{ H}_2\text{O}$$
 (4)

or

$$2 \text{ FeO}_4^{--} + 2 \text{ H}_2\text{O}_2 + 8 \text{ H}^+ \longrightarrow 2 \text{ Fe}^{++} + 3 \text{ O}_2 + 6 \text{ H}_2\text{O}$$
 (5)

with subsequent oxidation of the ferrous ion, or perhaps only decomposition of the ferrate ion by acid,

$$2 \text{ FeO}_4^{--} + 10 \text{ H}^+ \longrightarrow 2 \text{ Fe}^{+++} + 1^1/2 \text{ O}_2 + 5 \text{ H}_2\text{O}$$
 (6)

or

$$2 \text{ FeO}_4^{--} + 8 \text{ H}^+ \longrightarrow 2 \text{ Fe}^{++} + 2 \text{ O}_2 + 4 \text{ H}_2\text{O}$$
 (7)

Unfortunately no data are available for the free energy of formation of such substances as chromate, permanganate and ferrate ion. The only unknown value for calculating ΔF_{298}° for Reactions 3, 4, 5, 6 and 7 is that for FeO₄⁻⁻. By an application of the known data to Equations 3 and 4 we are led to the conclusion that F_{298}° must have a large negative

⁶ Bray, This Journal, 43, 1262 (1921); 45, 1251 (1923).

Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 607.

value, probably between -106,885 cals. and -182,155 cals. Whatever its value, since it is the same in all the reactions, it can be readily shown that the diminution in free energy is greater in Reactions 4 and 5 than in 6 and 7. This is in accord with the experimental result reported in the previous paper that the reduction of the ferrate ion takes place extremely readily in the presence of hydrogen peroxide. It can also be shown that ΔF_{208}° is greater in Reaction 4 than in Reaction 5, and greater in 6 than in 7, which leads to the conclusion that ferrous ion is less likely to be formed. We have shown experimentally that it is not present after the reaction is completed. It is also true that during the reaction the addition of a little potassium ferricyanide yields a blue precipitate, but this, in the presence of hydrogen peroxide, is at best very questionable evidence of the presence of ferrous salt (as pointed out by Mummery³) since the ferricyanide may be changed to ferrocyanide and react with the ferric salt.

Experimental Study of the Rate of Reaction

This opportunity is taken of very briefly describing the method of determining the rate of reaction under various conditions. This method, which was used also in obtaining some data on promoter action to be discussed in a subsequent paper, was fundamentally the same as that used in earlier studies, 4,9 with some modifications and improvements. The materials used were the same as in the earlier studies. The reaction was allowed to take place in a specially designed flask supported in a thermostat by a shaking device, and the gas evolved was measured in a buret kept at the same temperature as the thermostat. The catalyst solution in the flask having been allowed to attain the temperature of the bath, a known amount of Perhydrol (30% hydrogen peroxide) was dropped into it, the shaking begun, and the volume of gas evolved was measured at known time intervals. In order to avoid difficulties due to hydrolysis of the catalysts, concentrated acidified solutions of the latter were prepared; these were diluted just before using, in such a manner that a known excess of free acid was present in the reaction mixture.

Calculations—Explanations of Tables

As previously noted, 4 the reaction, due to disturbing effects, is not strictly monomolecular, the values obtained for "velocity constants" varying

 8 Making the following arbitrary assumptions regarding F_{299}° for FeO₄--, ΔF_{298}° for the several reactions is as follows.

		CALORI	ES				
F ₂₉₈	Reaction 3	4	5	6	7		
-110,000	- 6,230	-144,310	-97,120	-69,040	-43,060		
-140,000	- 66,230	- 84,310	-37,120	- 9,040	+13,060		
-170,000	-126,230	- 24,310	+22,280	+50,960	+73,060		

The largest value estimated is thus shown to be too large, as FeO_4^{--} is rapidly reduced in acid solution, even when hydrogen peroxide is not present.

⁹ Bohnson, J. Phys. Chem., 24, 677 (1920).

slightly as the reaction proceeds. For the purpose, therefore, of comparing the rates of decomposition under different conditions, a velocity constant was calculated only over the second quarter of each reaction. A typical experiment, data for which are given in Table I, will serve to illustrate this method of calculation. In this table, as in all subsequent ones, the following abbreviations are used:

t = Time in minutes; T = temperature; N = normality of free acid present; $C_{\text{Fe}} = \text{concentration of iron salt in milligram-atoms of iron per liter}$; $C_{\text{HeO}_2} = \text{concentration of hydrogen peroxide in millimoles per liter}$.

TABLE I

DATA FOR TYPICAL EXPERIMENT

 $T = 30^{\circ}$ N = 0.076 $C_{\text{Fe}} = 10.0$ $C_{\text{H2O2}} = 130$

Total volume of gas evolved, 46.4 cc.; in second quarter of reaction, 11.6 to 23.2 cc.; time for second quarter of reaction, 18.7 min.; $K_R=94$

t...... 0 4 10 18 24 28 Cc. of O₂ evolved...... 0 4.9 8.2 12.7 18.0 21.5 23.6 46.4

The volume of oxygen evolved was carefully plotted against the time in minutes, and by interpolation from this curve the time was determined in which the second 25% of gas was evolved. The total volume of gas evolved was determined by a simultaneous experiment using the same concentration of hydrogen peroxide but a much larger concentration of catalyst, which caused the reaction in this experiment to reach completion in a very short time.

The usual expression for the monomolecular velocity constant, 0.4343 $K=(1/t)\log{(a/(a-x))}$, now becomes greatly simplified (since a is always 75%, and a-x always 50% of the total gas evolution) to $K_1=(1/t)\log{(3/2)}$, or $K_1=0.1761/t$. To avoid decimals, this constant is multiplied by 10^4 , and the value so obtained called K_R . This method of expressing the rate of the reaction proved to have several advantages: (1) a shorter time was required to complete a set of experiments; (2) routine calculation was reduced to a minimum; (3) much closer duplication of results was secured than by averaging values obtained by the usual method, and (4) the figures obtained represent comparable conditions. It will be noted that the results obtained are in effect a comparison of the times necessary for the completion of equal fractions of the reaction under various conditions, and that K_R is a measure of the relative rate of the reaction.

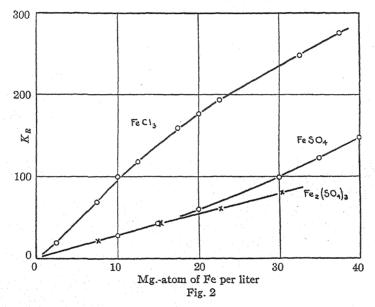
In order to save space, complete data for the remaining experiments are omitted, only summaries being given. The values reported for the velocity constants are supported by numerous other determinations, not given, of duplicate and intermediate values. There was no difficulty in checking within 3%.

Conditions of Experiment.—Unless otherwise noted, the concentration

of free acid was uniformly 0.076 N, that of the hydrogen peroxide 130 millimoles per liter, and the temperature 30°. All of von Bertalan's experiments were performed in complete darkness. This precaution having been found to be unnecessary, all of our experiments were performed in the diffused light of the laboratory.

The Effect of Ferrous Sulfate

It has already been shown¹ that the sulfates of both ferrous and ferric iron accelerate the decomposition of hydrogen peroxide, although less effectively than equivalent concentrations of either ferric chloride or nitrate. 4.10 It might be expected that equivalent concentrations of fer-



rous and ferric sulfates would have an identical effect; although von Bertalan worked with both these salts, his results do not shed much light on this particular problem. A more direct comparison of the effect of these two salts is possible by an examination of the data in Table II, which are shown graphically in Fig. 2.

Table II

Comparative Effects of Ferrous and Ferric Sulfates

		T_{\cdot}	= 30°	N = 0.076	C_1	$_{\rm H_{2}O_{2}}=1$	130	
	-Ferrous s	ulfate-				Ferri	sulfate-	
$C_{\mathbf{Fe}}$	K_R	$C_{\mathbf{Fe}}$	K_R		C_{Fe}	K_R	$C_{\mathbf{Fe}}$	K_R
10	28	30	99		7.6	21	30.4	81
15	43	35	123		15.2	43	60.8	156
20	60	40	148		22.8	60		

¹⁰ See also Fig. 2.

It will be noted that the curves for ferrous and ferric salts are coincident for concentrations of less than about 20 milligram-atoms of iron per liter, at which point the effect of the ferrous salt appears to become relatively and progressively greater. The reason for this divergence clearly lies in the fact that the ferrous sulfate is oxidized to ferric sulfate by the hydrogen peroxide, according to the equation, $2\text{FeSO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$, with a necessary decrease in the concentration of free sulfuric acid in the solution. The original concentration of acid being 0.076 N, it is evident that the oxidation of 20 millimoles or more of ferrous sulfate removes a relatively large proportion of the acid; since, as has been shown in other papers, free acid has a marked retarding effect on this catalysis, a decrease in its concentration causes an accelerated reaction. To this phenomenon is probably due the apparently greater catalytic effect of ferrous salt noted by Mummery.³

Von Bertalan claims to have found ferrous salt present after the completion of the reaction. This we did not find to be the case; on the contrary, when either ferrous or ferric salt is used as the catalyst, qualitative tests show it to be in the more highly oxidized form after the reaction is completed. During the progress of the reaction, the iron is present partly at least in a still higher state of oxidation. Quantitative measurements showed that in all cases in which ferrous sulfate was used as a catalyst, the volume of oxygen evolved was not equivalent to the amount of hydrogen peroxide used, a portion of the latter having been utilized in the oxidation of the iron. It is possible that a rapid method for the quantitative estimation of ferrous and ferric salts in the presence of each other might be based upon a measurement of the oxygen evolved from a given quantity of hydrogen peroxide.

It is incorrect, therefore, to speak of the catalytic effect of ferrous ion, which is oxidized instantaneously to ferric ion, and appears as such after the completion of the reaction; whatever accelerating effect it may have is due to the formation of the ferric salt. There seems to be need of further investigation of the action of hydrogen peroxide on certain alcohols and organic acids in the presence of ferric salts, which are reported to have no catalytic influence, ¹¹ while ferrous salts are said to have such an effect. Our preliminary experiments on this problem have led us to believe that ferric chloride at least is effective.

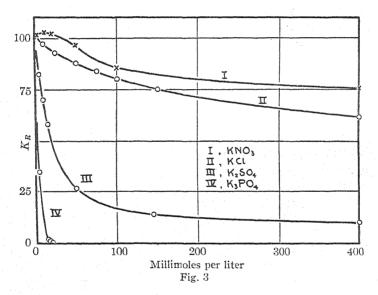
The Catalytic Effect of Non-ionized Salt

All previous work, as has been noted, was done with very dilute solutions of the iron salts. Von Bertalan, using only the sulfates, concluded that the rate of reaction was proportional to the concentration of iron ions.

¹¹ Fenton, J. Chem. Soc., **65**, 899 (1894). Fenton, Proc. Chem. Soc., **14**, 119 (1898). Doroschevski and Bardt, J. Russ. Phys. Chem. Soc., **46**, 754, 1669 (1914).

Duclaux, from an examination of our own previous work, concurred in this conclusion, even suggesting that this reaction is the best means of measuring the ionization and hydrolysis of iron salts, on the supposition that non-ionized salt is ineffective. This conclusion is supported by the facts that: (1) the effects of ferric chloride and nitrate in dilute solution are identical; (2) the suppression of ionization by added sodium or potassium salts is accompanied by a retardation of the reaction; (3) the addition of such a non-ionized salt as mercuric chloride had little or no effect, and (4) the products of hydrolysis had no effect.

On the other hand, the marked difference between the catalytic activities of ferric chloride and ferric sulfate is greater than might be expected from the different ionization of the two salts. This difference is more readily



explained by assuming that the molecular salt has an activity independent of that of the ions. Such an assumption would be in accord with a well-known hypothesis (the "dual theory" of catalysis) regarding catalytic processes, which has been discussed by a number of investigators.¹²

The curves shown in Fig. 3 (plotted from the data of Table III) represent the change in the catalytic activity of a constant concentration of ferric chloride (10 millimoles per liter) in the presence of increasing quantities of various neutral salts. One result of the addition of these salts is obviously the formation by metathesis of another ferric salt existing at least partly in the molecular state. In this connection a comparison of

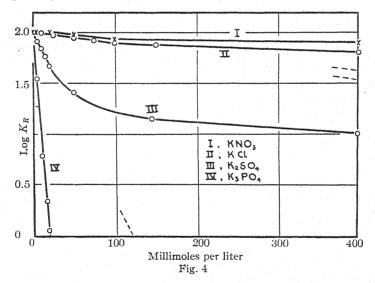
¹² See, among others, Acree, Am. Chem. J., 37, 410 (1907); 38, 258 (1907); 49, 353 (1913). Snethlage, Z. physik. Chem., 85, 255 (1913). Senter, J. Chem. Soc., 91, 467 (1907).

the curves indicates that the several molecular species vary in activity, the nitrate being most active. Another effect of the inhibiting salt would

Table III
Effect of Neutral Salts on Ferric Chloride Catalysis

	$C_{\rm Fe} = 10$.0					
	KC1	KN	O ₃	K_2	3O4	K ₃ F	1 O ⁴
C	K_R	C	K_R	С	K_R	C	K_R
0	100	0	100	. 0	100	0	100
10	98	2	101	5	82	1	82
25	93	5	103	10	70	5	35
50	88	10	103	15	58	10	6
75	83	20	102	20	47	16	$^{2.2}$
100	79	50	96	50	26	18	1.1
150	75	100	86	150	14	20	0.8
400	62	400	75	400	10		
		1880	60				

be the suppression of the ionization of the iron salt; however, the addition of a quantity of neutral salt 40 times as great as that of the ferric chloride



present is insufficient to inhibit the reaction completely. In the case of potassium nitrate, the addition of 188 times as much decreased the velocity constant only to 60, which represents a greater rate than would be expected on the supposition that iron ions alone are active. The rapid decrease in activity when potassium phosphate is added may be due to the removal of iron as a complex ferric-phosphate ion.¹³

It may be concluded, therefore, that in this reaction both the ions and the molecules are catalytically active.

¹³ Weinland and Ensgraber, Z. anorg. Chem., 84, 340 (1913).

In Fig. 4 the same data are plotted with the logarithms of K_R as ordinates. An examination of the curves thus obtained shows that they begin as straight lines, indicating that the first result of the addition of neutral salt is an exponential function of the concentration. The curve changes direction and proceeds again as a straight line with a different slope than formerly. A second effect is thus indicated, of smaller magnitude than the first one. These facts admit of two interpretations.

- 1. The first segment in the curve for all salts but potassium chloride may represent the metathetical reaction, while the second represents the suppression of the ionization of the newly formed salt. This hypothesis fails to explain the marked break¹⁵ in the potassium chloride curve. The single effect of the potassium phosphate curve is explained by the formation of a complex ion.
- 2. The two segments may represent two molecular forms of somewhat differing activity. The reason for such a difference is not clear, but the suggestion, which proves useful in a study of the accelerating effect of copper salts, will be discussed in a subsequent paper.

The Temperature Coefficient

In Table IV are shown the results of a number of experiments to determine the temperature coefficient of the reaction in the presence of

			I Al	31/14 T A			
Eff	ECT OF	Catalyst a	ND ACID	on the T	EMPERATU	re Coeff	ICIENT
$C_{\mathbf{Fe}}$	K_{400}	K_{30} 0	K_{200}	K_{40}/K_{80}	E_1	K_{30}/K_{20}	E_2
		(a) Fer	ric Chlori	ide N	= 0.076		
2.5	75	19.5	4.1	3.85	25,300	4.75	27,400
5	171	46	10.6	3.72	24,650	4.34	25,800
10	326	94		3.47	23,350		
20	607	177	43.5	3.43	23,140	4.07	24,670
50	1107	320		3.46	23,280		
		(b) Fer	ric Chlor	ide <i>I</i> V	= 0.038		
2.5	145	39.5		3.67	24,410		
5	321	89.3		3.60	24,010		
		(c) Fe	rric Sulfa	te N	= 0.076		
7.6	75	21	5.6	3.57	23,880	3.75	23,230
60.8	486	156	48.5	3.12	21,820	3.22	20,530
		Mean	value fo	E = 23	960 cals.		

different concentrations of catalyst and of acid. The results seem to be somewhat in accord with the assumption of the radiation hypothesis that "any agency which increases the reaction velocity diminishes the temperature coefficient," 16 although the decrease in values with increasing con-

¹⁴ These facts are more marked when all of our data are plotted on a large scale.

¹⁵ When copper salts are present in addition (markedly increasing the reaction rate), there is no break in the potassium chloride curve.

¹⁶ Lewis, J. Chem. Soc., 109, 796 (1916).

centration of catalyst is not particularly marked. It may be noted that the change of coefficient with temperature is not so great with sulfate as with chloride, the results for the former agreeing substantially with those of von Bertalan, who found $K_{40}/K_{30}=3.2$ and $K_{30}/K_{20}=3.3$.

In the columns E_1 and E_2 are shown the "critical increments" of the reaction according to the radiation hypothesis, calculated from the expression $\frac{d \log K}{dT} = \frac{E}{RT^2}$. The mean value of the critical increment is 23,960 cals. per mole of hydrogen peroxide decomposed; this, when substituted in the expression $E = Nh\nu$ gives 2.5×10^{14} for the frequency of the active radiation, the wave length of which would therefore be 1.2×10^{-4} cm. $= 1.2 \mu$.

Summary

- 1. This paper is a continuation of a former study of the catalytic decomposition of hydrogen peroxide by ferric salts. The existence of an intermediate compound, H₂FeO₄, previously suggested, has been confirmed by a spectroscopic examination of the reaction mixture.
- 2. The free energy of formation of ferrate ion, FeO_4^{--} , is shown to be in the neighborhood of -140,000 cals. Free-energy relationships show that the ferrous-ferric ion intermediate reactions postulated by von Bertalan are improbable.
- 3. The catalytic effect of ferrous salts is shown to be due solely to the fact that they are oxidized first to ferric salts.
- 4. The molecules of ferric salt, as well as the ions, appear to exert catalytic activity. It is possible that there are two molecular forms of differing activity.
- 5. The temperature coefficient of the reaction shows the "critical increment" of the reaction to be 23,960 cals., the frequency of the active radiation 2.5×10^{14} , and its wave length 1.2μ .

MADISON, WISCONSIN

[Contribution from the Laboratories of the Rockefeller Institute for Medical Research]

A WATER-JACKETED HYDROGEN ELECTRODE

By Henry S. Simms Received May 21, 1923

A hydrogen electrode cell has been designed to give rapid and accurate results and at the same time offer greater convenience in manipulation when working with certain fluids, than other types of cells. The results have been sufficiently satisfactory to warrant publication of a description of the cell.

¹⁷ For the methods of these calculations, see among others, Daniels and Johnston, This Journal, 43, 53, 72 (1921).

Description of Cell

This cell is kept at constant temperature by means of a water jacket through which water from a thermostatic bath is circulated. It has a 3-bore, 4-way stopcock which performs all the functions required. This stopcock is bored as shown in Fig. 1. The three bores do not intersect. Bore c is used in both Position III and Position IV. In order that both ends of Bore c may coincide with the opening of the arm for the salt bridge,

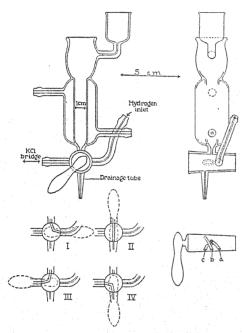


Fig. 1.—The water-jacketed hydrogen electrode cell. In Position I, Bore a connects the source of hydrogen with the cell; in Position II, Bore b connects the cell with the drainage tube; in Position III, Bore c connects the cell with the salt bridge; in Position IV, Bore c connects the salt bridge with the drainage tube. Order of manipulation: I, II, IV, III

this opening of the arm must be elliptical in shape. The cell may be constructed of either Pyrex or ordinary glass.

The Platinum Electrode is a spiral of platinized platinum wire sealed into a glass tube passing through a rubber stopper to the bottom of the cell. The tube contains mercury in order to make contact. stopper has a supplementary hole for the escape of hydrogen. Readings are taken with the electrode entirely immersed. The spiral serves, furthermore, to break up the bubbles of hydrogen, thus promoting rapid saturation. The electrodes are frequently changed and re-platinized. A fresh electrode must be saturated for a much longer period before the first reading is made. When not in use, the cell is kept filled with distilled water.

The Calomel Cell is constructed with a water jacket and has a platinum wire sealed into

the bottom and a mercury contact. In it are placed mercury, calomel and mercury, and a solution saturated with both potassium chloride and calomel. It is filled to the top and when the stopper is introduced the excess solution is forced out of the tube (which contains a loose plug of cotton), thus eliminating all air bubbles.

The Salt Bridge is "closed," that is, not open to the atmosphere's pressure. When the liquid junction is formed there can be no flow of liquid. Saturated potassium chloride solution is used to eliminate liquid junction

potential and, for convenience, is colored with α -azurine G. A reservoir (D) of this solution is kept at constant level by means of a glass tube connected with an inverted bottle of potassium chloride solution on a shelf above the apparatus, and is connected to the bridge by means of a stop-cock (E) which is kept closed by an elastic band attached to a glass hook fused to the stopcock handle. One liter of potassium chloride solution will serve as a supply for a year.

The Hydrogen, which is supplied from a tank with a reducing valve, is passed through water and then through a coil in the constant-temperature bath, from which it is brought to the electrode by means of Tube J. The

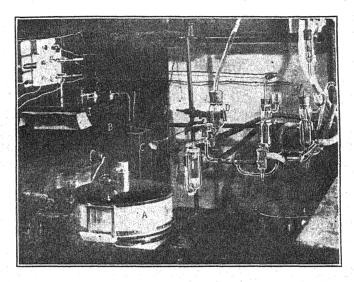


Fig. 2.—Hydrogen-ion apparatus. A. Potentiometer. B. Galvanometer. C. Storage battery, single cell. D. Constant level reservoir of saturated potassium chloride solution. E. Self-closing stopcock connecting the potassium chloride reservoir with the salt bridge. F. Water-jacketed calomel cell. G. Salt bridge. H. Hydrogen electrode cell (of a different type than described in this article). I. Hydrogen electrode cell described in this article. J. Hydrogen gas supply. K. Dish to collect drainage. L. Automatic nipple for distilled water supply

pressure of the hydrogen is regulated to about 6-7 mm. of mercury. This gives an even flow of small bubbles when the stopcock (in Position I) is partly opened.

Water Circulation from the bath through the cells is accomplished by means of an "air lift" which is merely a siphon system through the cells into which air is injected to raise the water back up to the bath. It is not essential for the functioning of the air lift that the bath be at a higher level than the cells. If the bath were on the same level as (or even below) the cells, the water after passing through them could be carried down to

the floor and then raised to the bath by means of the air lift, thus circulating the water.

Manipulation

The hydrogen electrode cell has but a single stopcock which performs the following functions. First, in Position I, it allows hydrogen to be bubbled through the apparatus (for three minutes). Second, in Position II, it permits a few drops of solution to drain, and thus remove all bubbles of hydrogen.1 Third, it is swung around (to the left) to Position IV, connecting the salt bridge with the drainage tube. Here no liquid can flow until Stopcock E is opened. Hence the stopcock of the cell is left open in Position IV while the operator reaches with the same hand to open Stopcock E, permitting a few drops of potassium chloride solution to drain. Thereafter it is necessary merely to release the Stopcock E, since it closes automatically. This procedure has filled Bore c of the cell stopcock with potassium chloride solution. Fourth, it is then turned to Position III, thus forming the liquid junction, and a reading is taken. If another reading is desired, the stopcock is turned to Position II, where a few drops of solution are allowed to drain, and then turned to Position I, where the saturation with hydrogen is continued.

Discussion

This cell has the following advantages.

- 1. Its temperature may be accurately controlled without interfering with its manipulation. It may be more conveniently handled than is the case with cells placed in an air or oil thermostat.
- 2. The temperature of the cell is maintained with such constancy that a solution which is much colder or much warmer than the cell will be brought to the desired temperature during the three minutes required for saturation. Thus, a solution may be taken from the refrigerator and introduced directly into the cell without being previously warmed.
- 3. One stopcock performs all the functions required, thus preventing accidental passage of gas into the salt bridge or of potassium chloride solution into the cell.
- 4. The closed bridge prevents mechanical agitation when the liquid junction is formed.
- 5. The liquid junction is only 6 mm. from the platinum electrode, thus permitting accurate readings even with solutions of low conductivity.
 - 6. One to two cc. of solution is sufficient for 2 to 6 consecutive readings. Accuracy.—Bubbling with hydrogen for three minutes gives readings
- ¹ In case the drainage of the solution (in Position II) is stopped by bubbles, the hole in the rubber stopper is closed with the forefinger of the left hand, while the fleshy portion of the right thumb is gently pressed on the filling cup of the cell. The pressure created will start the flow of liquid.

which do not change more than 0.1 to 0.2 millivolt even after two hours' bubbling. Readings are reproducible to $0.01~P\pi$.

The fact that the whole system is not at the same temperature should produce no appreciable error, since the liquid junction is at practically the same temperature as the electrodes and no potential can be produced by temperature variations in the bridge.

The "open stopcock" junction is subject to the usual errors.

Summary

A simple water-jacketed hydrogen electrode cell of the bubbling type is described which is accurately maintained at constant temperature with water from a bath, circulated by means of an air lift.

It gives accurate readings reproducible to 0.01 PH with 1 or 2 cc. of solution after three minutes' saturation with hydrogen, even with solutions of low conductivity.

It has a single stopcock which performs separately the following functions: It permits (1) bubbling of hydrogen gas through the solution; (2) drainage of solution; (3) drainage of potassium chloride solution from the salt bridge; (4) formation of liquid junction.

NEW YORK, N. Y.

[Contribution from the Department of Chemistry of the Massachusetts Institute of Technology]

THE FREE ENERGY OF MERCURIDES

By Roscoe H. Gerke Received May 26, 1923

Alloys and metallic compounds are important classes of substances for which there are few free-energy data. It is the purpose of this paper to collect available data on metallic compounds and solid solutions containing mercury, and incidentally point out that the method of calculating these quantities involves the use of partial molal free energy. Hitherto, the concept of partial molal free energy has not been used to split up the free energy of formation of a compound from its constituent elements into two parts, as has been done in this paper. In the case of the mercurides and other metallic compounds, it will be seen that the free energy of formation of the compound from its elements is equal to the sum of the separate free-energy changes which the elements undergo in the formation of the compound.

In the case of sodium mercuride, NaHg₅, the partial molal free energy \overline{F}_2 , of the sodium in the compound is measured by the electromotive force of the galvanic cell, Na(s) | Na⁺ | Na in Hg + NaHg₅(s). The chemical equa-

¹ The notation employed is that of Lewis and Randall, This Journal, 43, 233 (1921).

tions which represent the change of state attending the passage of electricity through the cell are as follows.

Equation 3 represents the sum of Equations 1b, 2a and 2b. It represents the change in state in the formation of one gram-atom of sodium in the compound and the corresponding change of free energy is equal to the partial molal free energy of one gram-atom of sodium, \overline{F}_2 , in the compound, since the change of free energy in an equilibrium process is zero and the free energy of an element in its standard state is taken as zero.

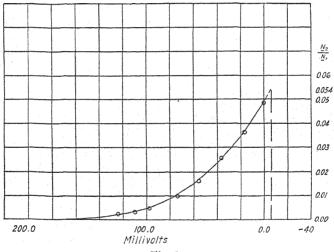


Fig. 1

If the free energy of dilution of the sodium in the mercury amalgam has been measured at various dilutions, then the partial molal free energy of the mercury, \overline{F}_1 , in the compound may be determined with the aid of the Gibbs equation, $d\overline{F}_1 = -\frac{N_2}{N_1}d\overline{F}_2$, which when integrated takes the form, $\overline{F}_1 - F_{(Hgl)} = \overline{F}_1 = +nf \int \frac{N_2}{N_1}dE$, where E is the electromotive force of galvanic cells similar to the one previously described, with different concentrations of electropositive metal in the dilute amalgams.

The integration is most conveniently carried out by plotting as ordinates the electromotive force and as abscissas the corresponding ratio, N_2/N_1 of the mole fractions of the constituents of the liquid amalgams. In Fig. 1

the data² for dil. sodium amalgams are plotted. A small extrapolation to the saturated amalgam, $N_2/N_1 = 0.054$, is indicated by the dotted line. The limits of the integration for N_2/N_1 are 0 and 0.054, respectively, and for E they are $+\infty$ and -6 millivolts, respectively. The area under the curve multiplied by the proper factor to convert to calories is equal to the change in free energy when one gram-atom of liquid mercury reacts to form one gram-atom of mercury in the liquid amalgam, which in turn is equal to the partial molal free energy of one mole of mercury in the compound, since the free energy of the liquid mercury is zero.

The free energy of sodium mercuride was calculated as follows,

$$Na(s) = Na \text{ (in NaHg5); } \Delta F = \overline{F}_2$$
 (4)

$$5 \text{Hg(I)} = 5 \text{Hg (in NaHg5)}; \Delta F = 5 \overline{F}_1$$
 (5)

$$Na(s) + 5Hg(1) = NaHg_5(s); \Delta F^{\circ} = \overline{F}_2 + 5\overline{F}_1$$
 (6)

In Table I are shown the free energies of formation of the mercurides of sodium and lead.

Table I
Free Energy of Formation of Mercurides of Sodium and Lead

N ₂ (sat.) °C.	E.m.f.	$\overline{\mathbf{F}}_{2}$	$\overline{\mathbf{F}}_{1}$	ΔF°	Compound
0.054^a 25	0.7821 ^b -	18,046	-61°	-18,351	$NaHg_5^d$
0.017 30	0.0058 ^f	- 134	-12^{g}	- 280	Pb_2Hg^e

In Table I, a corresponds to References 3, 6; b to 2, 3, 4, 5; c to 2; d to 6; e to 7; f to 8; g to 9.

The mole fraction, N_2 (sat.), of the more electropositive metal in the liquid amalgam saturated with the compound is listed in Col. 1; the centigrade temperature in Col. 2; the electromotive force in volts of the galvanic cell, corresponding to Equation 1, in Col. 3; the partial molal free energy, \overline{F}_2 , in calories of one gram-atom of the more electropositive metal in the compound in Col. 4; the partial molal free energy \overline{F}_1 in calories of one gram-atom of mercury in the compound, in Col. 5; and finally the free energy of formation ΔF° , of one mole of the compound in Col. 6. (The footnotes refer to the sources from which the data were taken.)

In Table II are collected the partial molal free energies of metals in the mercurides of lithium, potassium and rubidium. Since the free energies of dilution of these electropositive metals in mercury amalgams have not been measured, the partial molal free energy, 10 \overline{F}_1 , of the mercury was

- ² Richards and Conant, This Journal, 44, 601 (1922).
- ³ Danner, ibid. 44, 2832 (1922).
- * Lewis and Kraus, ibid., 32, 1459 (1910).
- ⁵ Allmand and Polack, J. Chem. Soc., 115, 1020 (1919).
- ⁶ Smith and Bennett, This Journal, 32, 622 (1910).
- ⁷ Fay and North, Am. Chem. J., 25, 216 (1901).
- ⁸ Gerke, This Journal, 44, 1684 (1922).
- ⁹ Richards and Garrod-Thomas, Z. physik. Chem., 72, 165 (1910).
- 10 It is nearer to the truth to make this assumption than to calculate this quantity from the equation $\vec{F}_1 = RT \ln N_1$ assuming that Raoult's law is valid, since this calculation gives -30 calories as the value of the partial molal free energy of one mole of mercury in sodium mercuride, instead of the value -61 calories in Table I Since the

assumed to be the same as that in the case of sodium. Also, the liquid amalgams in the galvanic cells were not saturated with the solid compounds, as in the case of the sodium and lead mercurides. The small correction could be calculated and subtracted from the measured values, but since the measured values for the dilute amalgams are of such high precision, it may be well to insert them in the table as they appear in the literature.

Table II

Partial Molal Free Energy of Alkali Metal Mercurides at 25°

N ₂ (sat.)	N_2 (dil.)	E.m.f. (dil.)	F ₂	$\overline{\mathbf{F}}_{1}$	Mercuride
0.02^{11}	0.0087	0.9502^{12}	-21,900	(-61)	${ m LiHg_3}^6$
.0313	.011	1.048114	-24,200	(-61)	$\mathrm{KHg_{12}}^{6}$
.0315	.0054	1.0745^{16}	-24,800	(-61)	$RbHg_{12}^{6}$

In Table II are listed, respectively, N_2 sat., the mole fraction of the electropositive metal in the saturated amalgam; N_2 dil., the composition of the dil. amalgam actually employed in the cells; e.m.f. dil., the electromotive force, in volts, of the cell, the electrodes of which are solid electropositive metal and dil. amalgam; \overline{F}_2 and \overline{F}_1 are the approximate partial molal free energies in calories of one gram-atom of the electropositive-constituent and of one gram-atom of mercury in the compound, respectively.

TABLE III

PARTIAL MOLAL FREE ENERGY OF METALS AND OF MERCURY IN MIXED CRYSTALS

Na (sat.)	°C.	E.m.f.	$\overline{\mathbf{F}}_{2}$	$\overline{\mathbf{F}}_{\mathbf{i}}$	Mixed crystals
0.07	25	0.0047 ^h	-215	- 35°	Zn in Hg
10^{i}	25	.0505 ^k	-2330	- 77 ¹	Cd in Hg
.43**	20	$.0022^{n}$	- 51	-523°	Tl in Hg

In Table III, g corresponds to references 17, 18, 19; h to 20, 21; i to 22, 23, 24; j to 19; k to 19, 20, 22, 25, 26; l to 24, 27; m to 28; n to 28, 29, 8; o to 1, 28.

mole fraction, N_1 , of the mercury in these cases in Table II is greater than that in the case of sodium mercuride in Table I, the partial molar free energies, \overline{F}_1 , of one mole of mercury in Table II are certainly not greater than, and in all probability are less than the value, -61 calories.

- ¹¹ Zukowsky, Z. anorg. Chem., 71, 409 (1911).
- 12 Lewis and Keyes, This Journal, 35, 340 (1913).
- 13 Janeke, Z. physik. Chem., 58, 245 (1907).
- 14 Lewis and Keyes, This Journal, 34, 119 (1912).
- 15 Kurnakow and Zukowsky, Z. anorg. Chem., 52, 427 (1907).
- 16 Lewis and Argo, This Journal, 37, 1983 (1915).
- 17 Puschin, Z. anorg. Chem., 36, 214 (1903).
- ¹⁸ Cohen and Ginnekin, Z. physik. Chem., 75, 437 (1911).
- 19 Cohen and Moesvald, ibid., 95, 285 (1920).
- ²⁰ Richards and Lewis, *ibid.*, 28, 1 (1899).
- ²¹ Cohen and Tombrock, Verslag. Akad. Wetenschappen Amsterdam, 18, 17 (1909).
- ²² Cohen, Z. physik. Chem., 34, 612 (1900).
- ²³ Crenshaw, J. Phys. Chem., 14, 158 (1910).
- ²⁴ Richards and Forbes, Z. physik. Chem., 58, 683 (1907).
- ²⁵ Hulett, Trans. Am. Electrochem. Soc., 7, 353 (1905).
- ²⁶ Obata, Proc. Phys. Math. Soc. Japan, [3] 3, 64 (1921).
- " Hulett and DeLury, This Journal, 30, 1812 (1908).
- 28 Richards and Daniels, ibid., 41, 2452 (1919).
- 29 Richards and Smyth, ibid., 44, 324 (1922).

In Table III are listed precise partial molal free energies of one gramatom of the constituents of mixed crystals, in order to compare them with the partial molal free energy of the constituents of compounds.

Discussion

The conventions have been such that the free energy of formation, $\Delta F^0 = -18,351$ calories, means that there has been a decrease at 25° and 1 atm. of free energy attending the formation of one mole of NaHg₅ from one atom of sodium and 5 atoms of mercury. This decrease has been divided between the decrease for the sodium and the mercury respectively, such that \overline{F}_2 equals -18,046 calories and \overline{F}_1 equals 61 calories per atom. It is to be noted that the more electropositive the metal, the greater is the free-energy change, except in the case of lithium.

The most striking and unexpected conclusion which can be drawn from these data, is that the mercury does not greatly change in free energy, when it enters into chemical combination with a more electropositive metal. In other words, the vapor pressure of pure liquid mercury is only very slightly greater than the partial pressure of mercury from an amalgam saturated with a mercuride. On the other hand, the electropositive metal decreases in free energy more than the mercury in the formation of the compounds. In the case of the mixed crystals, thallium is an exception, which possibly may be due to the fact that it is so close to mercury in the periodic table of the elements.

Although the free energy of other metallic compounds and also compounds of the type represented by iodine chloride can be calculated by the above method, it does not seem feasible to make similar measurements for a simple compound such as sodium chloride, since it is not possible to have solid sodium chloride in equilibrium with its solution of sodium in liquid chlorine.

In conclusion, it may be stated that, if mercury reacts with a more electropositive metal to form a mercuride, the change in free energy for the mercury is small compared with that of the more electropositive metal.

The author wishes to express his appreciation for the helpful criticism of Dr. L. J. Gillespie and Dr. E. B. Millard.

Summary

- 1. The partial molal free energy of the electropositive atom in a mercuride or a mixed crystal containing mercury has been calculated from the measured value of the electromotive force of a galvanic cell, the electrodes of which consist of the electropositive metal and the liquid amalgam saturated with the mercuride or mixed crystal.
- 2. The values for the partial molal free energies of rubidium, potassium, lithium, sodium and lead in their mercurides have been found to be -24,800, -24,200, -21,900, -18,046 and -134 calories, respectively.

- 3. The partial molal free energy of mercury in some mercurides has been calculated from the measured values of the electromotive force of amalgam concentration cells.
- 4. The values for the partial molal free energy of mercury in sodium and lead mercurides were found to be —61 and —12 calories, respectively.
- 5. The free energies of formation of sodium and lead mercurides are —18,351 and —280 calories, respectively.
- 6. The partial molal free energies of the constituents of mixed crystals of zinc-mercury, cadmium-mercury and thallium-mercury crystals have been tabulated.
- 7. With the exception of thallium, it has been found in the case of the mercurides and the mixed crystals studied, that the change in free energy has been greater for the electropositive metals than for mercury.

Cambridge 39, Massachusetts

[Contribution from the Laboratories of General Chemistry of the University of Wisconsin]

PROMOTER ACTION IN HOMOGENEOUS CATALYSIS. I. COPPER SALTS AS PROMOTERS IN THE IRON SALT CATALYSIS OF HYDROGEN PEROXIDE

By Van L. Bohnson and A. C. Robertson Received June 11, 1923

The investigation described in this paper was an outgrowth of an earlier study^{1,2} of the catalytic decomposition of hydrogen peroxide, during which it was noted that the rate of evolution of oxygen in the presence of a mixture of iron and copper salts is much more rapid than the rate which may be calculated on the assumption that each salt acts independently. This phenomenon is analogous to what has been known in cases of heterogeneous catalysis as "promoter action." The latter designation, first used in the patents of the Badische Anilin und Soda Fabrik, might well include, according to Pease and Taylor,3 all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the assumption that each substance in the mixture acts independently. So defined, the term is applicable not only to cases of heterogeneous catalysis, to which it was first applied, but also to homogeneous catalysis, and in this sense it is used in this paper; such a use is no intimation that the mechanism of reaction in the two different systems is the same.

The known examples of promoter action have been reviewed and classified by Pease and Taylor,³ and therefore will not be described here. Ex-

¹ Bohnson, J. Phys. Chem., 25, 19 (1921).

² Bohnson and Robertson, This Journal, 45, 2493 (1923).

³ Pease and Taylor, J. Phys. Chem., 24, 241 (1920).

amples in the field of homogeneous catalysis are relatively few in number, the one best known being the effect of neutral salts in accelerating the acid-catalyzed hydrolysis of esters. Two reactions which are of interest in connection with the present study are the oxidation of potassium iodide by potassium persulfate, and the reaction between hydrogen peroxide and hydriodic acid; in both of these cases the reaction was "promoted" by the action of copper salts in the presence of iron salts.

Purpose and Method

In an attempt to outline in a preliminary way the mechanism of promotion, this paper will be devoted to a discussion of the factors involved in the accelerating effect of copper salts upon the iron-salt catalysis of hydrogen peroxide in acid solution. Further papers will deal with promoter action in other homogeneous reactions, such as the activation of chromic acid and its salts (catalyzing the decomposition of hydrogen peroxide) by certain cations, a reaction which is now being studied in this Laboratory.

It has been suggested by Pease and Taylor³ that a distinction be made between simple "activation" of one catalyst by another substance not itself a catalyst for the reaction in question, and "co-activation," in which the catalytic effect of each active substance is increased by their joint presence. From this point of view, it is possible with the reaction in question that (1) the copper salt may be activated by the iron salt, (2) the iron may be activated by the copper, or (3) the two may activate each other. It is not always easy to decide among such hypotheses, but a determination of the promotion effect in the presence of various amounts of iron or copper may enable us to exclude certain of them, on the reasonable expectation that in any activation of one substance by another there is a limit to the accelerating effect of the primary catalyst when all the catalytic material has been "activated."

The method used for measuring the rate of reaction has been previously described.² The results obtained are merely summarized as in the previous paper, and are supported by numerous duplicates and intermediate values. In the tables the following abbreviations are used: T, temperature; N, normality of free acid present; $C_{\rm Fe}$, concentration of iron salt in milligram-atoms of iron per liter; $C_{\rm Cu}$, concentration of copper salt in milligram-atoms of copper per liter; K_R , the relative rate of reaction (see p. 2497 of preceding paper). In all experiments, unless otherwise noted, the concentration of free acid was 0.076 N, that of the hydrogen peroxide 130 millimoles per liter, and the temperature 30°. All experiments were performed in the diffused light of the laboratory, after it was

⁴ Price, Z. phys. Chem., 27, 499 (1893).

⁵ Brode, ibid., 37, 257 (1908).

found that those performed in darkness were not retarded either in the presence of iron alone or of iron and copper together.

Preliminary Experiments

Ferric chloride in solution exerts an energetic decomposing effect on hydrogen peroxide even in the presence of hydrochloric acid, which retards the catalysis materially. Ferric sulfate in sulfuric acid solution has a marked effect, less than that of the chloride. On the other hand, much larger quantities of cupric chloride, either in acid or in neutral solution, have very little noticeable effect. In fact, the salts of few other metals act as vigorously as the iron salts. When, however, small amounts of copper salt are mixed with the iron salt, the rate of reaction is very markedly increased. This effect seems to be peculiar to copper compounds; nickel, cadmium, mercury, barium, lead, cobalt, zinc, tin, and magnesium salts appear to retard rather than accelerate the reaction. In sulfate systems silver appears to have a very slight accelerating effect.

Effect of a Fixed Concentration of Copper in the Presence of Variable Iron Concentration

Fig. 1 shows graphically the relation between the rates of reaction caused by each salt alone and by mixtures containing various fixed concentrations

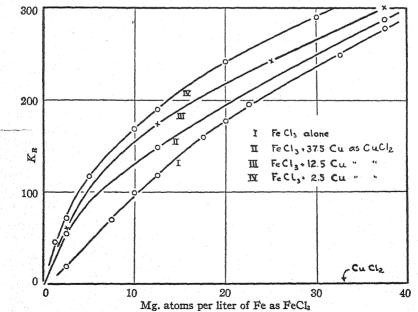


Fig. 1.—Effect on reaction rate of fixed copper with varying iron concentration of copper salt and varying concentrations of iron salt; the data for the curves are given in Tables I and II. In all these experiments the chlorides were used; the effect in sulfate systems will be considered later.

Table I

Comparison of Catalytic Effect of Ferric and Copper Chlorides

T = 20° N = 0.075

			1 - 50	71	0.010			
$C_{\mathbf{Fe}}$	CCu	K_R	$C_{\mathbf{Fe}}$	C_{Cu}	K_R	$C_{\mathbf{Fe}}$	C_{Cu}	K_R
0	32.5	0.63	7.5	0	69	20	0	177
0	37.5	1.16	10	0	100	22.5	0	195
0	50	1.8	12.5	0	118	32.5	0	248
2.5	0	19.5	17.5	0	160	37.5	0	276

TABLE II

Effect on the Rate of Reaction of Varying the Ferric Chloride Concentration

		T =	: 30°	N = 0.076	Chlorides		
$C_{\mathbf{Cu}}$	2.5	Ccu	= 2.5	Co	u = 12.5	$C_{Cu} =$	37.5
$C_{\mathbf{Fe}}$	K_R	C_{Fe}	K_R	C_{Fe}	K_R	$C_{\mathbf{Fe}}$	K_R
1.25	46	15	207	2.5	61	2.5	55
2.5	71	20	241	12.5	174	12.5	148
5	117	30	289	20	224	37.5	286
10	169	35	317	25	241		
12.5	190			37.5	300	• •	,

The curve for cupric chloride alone may scarcely be distinguished from the horizontal axis; therefore, on the assumption that the joint effect of iron and copper salts is purely additive, the curve for this joint effect should coincide with the curve for ferric chloride alone. It will be noted, however, that the presence of only a small amount of copper salt causes a marked acceleration. A large concentration of copper, as shown by Curves II and III, has a smaller effect; it is therefore evident that some concentration of copper in the vicinity of 2.5 milligram-atoms per liter is more effective than any other. From these results we may exclude the hypothesis that the copper salt is activated by the iron.

Effect of a Varying Concentration of Copper with a Fixed Concentration of Iron

That there is a maximum effective concentration of copper salt is better illustrated by the results shown in Figs. 2 and 3 (Tables III and IV). The curves represent the variation in the rate of reaction caused by varying concentration of copper salt in the presence of different fixed concentrations of iron salt. A relatively minute amount of copper has a marked effect, but in each case a maximum rate of reaction is obtained with a concentration of only 1 milligram-atom per liter. Beyond this point, the rate continually decreases with the addition of more copper, an effect which is quite analogous to that caused by the addition of sodium chloride. The maximum effective concentration of copper appears to be independent of the concentration of iron salt.

Table III

Effect of a Varying Concentration of Copper Chloride on the Rate of Reaction

			$T = 30^{\circ}$			N = 0.076		
	$C_{\text{Fe}} =$	2.5		C _{Fe} ≈	: 10		$C_{\text{Fe}} =$	20
	$C_{\mathbf{Cu}}$	K_R		C_{Cu}	K_R		C_{Cu}	K_R
	0	19.5		0	100		0	177
	0.05	44		0.05	135		0.1	224
ŕ	0.2	63		0.1	146		0.2	233
	0.375	66		0.2	159		0.3	238
	0.5	68		0.25	165		0.5	243
	1.0	68		0.75	174		0.875	244
	2.5	71		1.0	174		1.5	244
	12.5	61		1.25	173		2.5	241
	37.5	55		2.0	173		5.0	240
				2.5	169		30	191
				4.0	166			
				40	133			

TABLE IV

Effect of a Varying Concentration of Copper Sulfate on the Rate of Reaction

			1 ==	30		
N =	0.076		N = 1	0.076	N = 1	0.038
C_{Fe} =	= 7.6		$C_{\text{Fe}} =$	30.4	$C_{\rm Fe} = 7.6$	
$C_{\mathbf{Cu}}$	K_R		C_{Cu}	K_R	$C_{\mathbf{Cu}}$	K_R
0	21	•	0	81	0	35
0.1	76		0.1	210	0.1	126
0.3	98		0.2	255.	0.3	166
0.4	107		0.3	282	0.5	184
0.6	113		0.5	301	1.0	197
1.0	122		1.0	316	1.5	202
2.0	120		2.0	317	2.0	202
4.0	118		3.0	314		·
			5.0	291		

That the effect is common to both chloride and sulfate systems is evident; the maximum concentration of copper in each case is of the same order of magnitude, although ferric sulfate is a much less active catalyst than ferric chloride. It is also evident (Curve II, Fig. 3, and last column, Table IV) that the maximum effective concentration of copper is not altered by a large decrease in the concentration of the free acid present. These results lead to the conclusion that the iron salt is activated by the presence of a copper salt.

Conditions Affecting the Extent of Promotion

Promotion Factors.—It has been shown that for any given concentration of iron, a maximum rate of reaction is obtained with approximately the same absolute concentration of copper in all cases. By dividing the maximum rate by the normal rate for the given concentration of iron, a ratio is obtained which may conveniently be termed the "promotion

factor;" this factor represents the extent of promotion under given conditions.

Effect of Concentration of Catalyst.—The promotion factors for different concentrations of iron salt can be calculated from the values obtained

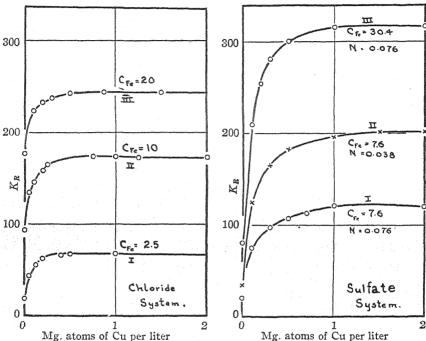


Fig. 2.—Effect on reaction rate of fixed iron with varying copper concentration iron with varying copper concentration

by interpolation from the curves of Fig. 1 and Fig. 4. The latter, for which the data are shown in Table V, represents the promotion process when sulfates of iron and copper are used (in the presence of free sulfuric acid).

Table V
Effect of a Varying Concentration of Ferric Sulfate

$C_{ extsf{Fe}}$	3.8	7.6	15.2	22.8	30.4	38.0	60.8
K_R : no Cu		21	43	60	81		156
K_R : $C_{Cu} = 1.0$	72.5		200	263	320	366	

TABLE VI

VARIATION OF PROMOTION FACTORS WITH CONCENTRATION OF IRON SALT

C_{Fe}	Promotion Chlorides	n factors Sulfates	C_{Fe}	Promotion Chlorides	n factors Sulfates
1	5.0	8.0	15	1.5	4.9
2	3.6	7.0	20	1.3	4.6
4	2.7	6.7	25	1.2	4.2
.7	2.1	6.0	30	1.2	4.0
10	1.7	5.6	40	1.17	••

In this case, as is shown also in the last column of Table VI, the promotion factor is much larger than in the chloride system, although the normal rate is less.

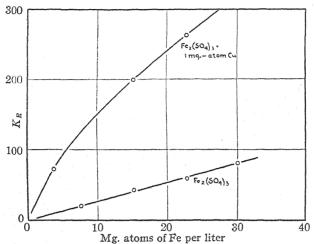


Fig. 4.—Effect on reaction rate of fixed copper with varying iron concentration

In both systems the promotion factor decreases as the concentration of iron salt increases, probably approaching 1 as a limiting value. This

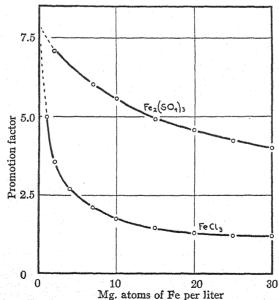


Fig. 5—Effect on the promotion factor of varying the concentration of primary catalyst is shown graphically in Fig. 5; it appears that the promotion factors for the two systems approach each other in magnitude as the concentration

of catalyst is decreased, thus indicating that in very dilute solutions of the catalyst the mechanism of promotion is independent of the nature of the anion.

It may be noted here that the promotion factor is the same when ferrous sulfate is the catalyst as when ferric sulfate is used, in dilute solution.

This fact is in accord with the initial 300 rapid oxidation of ferrous sulfate, discussed in the previous paper.

Effect of Concentration of Free Acid.—The effect of acid on the promoter action has already been partly shown in Curve II, Fig. 3, where it is seen that in the sulfate system the maximum effective concentration of copper is not changed by a decrease in the acid concentration: it can be shown that the promotion factor for $C_{\rm Fe} = 7.6$ is 5.8 whether the acid concentration is 0.038 N or 0.076 N. Similarly, for the chloride system, the promotion factor also remains unaltered when the concentration of free acid is changed from 0.076 N to 0.038 N. This is shown by the data of Tables VII and VIII, and in the curves of Fig. 6. The promotion factors obtained by interpolation from the latter are compared in Table VIII with those obtained from Fig. 1.

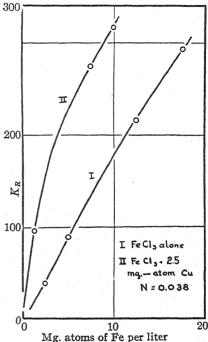


Fig. 6.—Promoter effect in the presence of decreased acid concentration

The fact that free acid has the same effect on the accelerated reaction that it has in the presence of iron salt alone, further confirms the hypothesis that the iron salt is the primary catalyst and the copper salt the promoter.

TABLE VII

EFFECT OF DECREASED ACID CONCENTRATION ON THE FERRIC CHLORIDE-COPPER CHLORIDE CATALYSIS

		T = 3	0 N =	0.038				
CFe	2.5	5	12.5	17.5	1.25	7.5	10	
$C_{\mathtt{Cu}}$	0	0	0	0	2.5	2.5	2.5	
K_R	39.5	89	216	293	96	275	317	

TABLE VIII

EFFECT	OF DECREAS	SED ACID CO	NCENTRATION (on Promotio	n Factors
C_{Fe}		on factors $N = 0.038$	$C_{\mathbf{Fe}}$		ion factors $N = 0.038$
2	3.6	3.5	7	2.1	2.1
4	9.7	2.7	10	1 7	1.8

Effect of Temperature.—The effect of temperature on the extent of promotion is also negligible. It is shown in Table IX that the promotion factor in the chloride system remains constant, even though the reaction rate is greatly increased by raising the temperature. That the temperature coefficient is unchanged by the presence of copper is shown by Table X; this is again evidence for the hypothesis that the copper salt present activates the iron salt.

Table IX

Effect of Temperature on Promotion Factors

 $R_n=$ normal rate, with ferric chloride; $R_p=$ rate when copper is present; P= promotion factor

		$-T = 40^{\circ}$	·	$\overline{}$	' = 30°			$-T = 20^{\circ}$	
$C_{\mathbf{Fe}}$	R_n	R_p	P	R_n	R_{p}	\boldsymbol{P}	R_n	R_{p}	P
$^{2.5}$	75	275	3.7	19.5	71	3.6	4.1	15.1	3.7
5	171	417	2.4	46	118	2.6	10.6	25.5	2.4
10	326	587	1.8	98	173	1.8			

Table X
Effect of Promoter on Temperature Coefficients

		Temperatur	e coefficients	
C_{Fe}	40/30 Fe a	alone 30/2	Fe : 40/30	= Cu 30/20
2.5	3.85	4.75	3.87	4.70
5	3.72	4.34	3.54	4.63
10	3.47	• •	3.40	

Effect of the Anion.—The effect on the reaction rate of the addition of various potassium salts to the reaction mixture when iron salts alone are

Table XI

Effect of Neutral Salts on the Promoter Action $T=30^{\circ}$ N=0.076 $C_{\rm Fe}({\rm as~FeCl_s})=10.0$ $C_{\rm Cu}=1.1$ $C_{\rm u}=0.00$ conen. of neutral salt in millimoles per liter

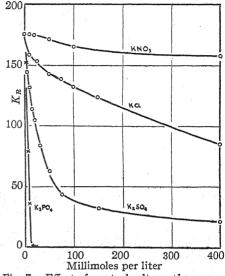
	Maximum rate, K_R								
C_s	KCI	KNO	K2SO4	K ₃ PO ₄					
0	176	176	176	176					
1		• • •		150					
5	• • •		145	76					
10	159	176	132	33					
15		• • •	114						
16	• • •	• • •		1.2					
18			A	0.8					
20	•••	175	105	0.6					
25	153								
30	• • •		84						
50	142	171	62						
75	138		44						
100	132	165							
150	124		32						
400	86	157	25						
1880		136							

the catalysts, has been shown in a previous paper. The effect of such salts when copper is present as a promoter is shown in Fig. 7, the data being given in Table XI. A comparison of these results, plotted logarithmically,

with those presented in the previous paper shows that the rate due to molecular salt is accelerated, as well as the rate due to iron ions.

The Mechanism of Activation

It was shown in the previous paper² that the decomposition of hydrogen peroxide by iron salts 100 alone is due to the formation and subsequent reduction by hydrogen peroxide of an intermediate compound, probably H₂FeO₄. The rate of evolution of oxygen from a given concentration of hydrogen peroxide is proportional to the concentration of the intermediate compound, which is in turn dependent upon the concentration of iron salt and Fig. 7.—Effect of neutral salts on the promoof acid, and differs notably, de-



ter action

pending upon whether the chloride, sulfate or nitrate of iron is used. other words, the rate of reaction measured by the gasometric method can be no faster than the slower of the intermediate reactions, whether this be the formation of ferric acid, or its reduction by hydrogen peroxide, or some step in these processes. It is conceivable that the promoter, which is thus a secondary catalyst, might accelerate either one or both of the intermediate processes.

Two equal portions of a solution of barium ferrate in acetic acid were allowed to react with equal quantities of hydrogen peroxide. To one of the samples a very little copper acetate was added; measurements of the oxygen evolved showed that this one reacted much faster than the one to which no copper salt was added. This is an indication that the copper accelerates the reduction of the intermediate compound.

This experiment is not sufficient to explain the noticeable fact (compare Fig. 1 with Fig. 4) that although the rate for a given iron concentration is much lower when the sulfate is used, the maximum "promoted" rate is very close to that obtained when the chloride is used. If, however, we assume that the copper salt also accelerates the formation of the intermediate compound, the facts are more easily understood. It is probable, therefore, that the copper acts as a secondary catalyst, accelerating both the intermediate reactions. The exact mechanism of this secondary catalysis is not yet clear.

Summary

- 1. A small amount of copper salt greatly accelerates the decomposition of hydrogen peroxide by iron salts in acid solution. Other metallic salts do not appear to have this "promoter effect."
- 2. For a given concentration of iron salt, either sulfate or chloride, there is a maximum rate of reaction with about 1 millimole per liter of added copper salt. This maximum effective concentration of copper appears to be independent of the concentration of iron salt.
- 3. The extent of promotion (measured by the "promotion factor," which is the ratio of the maximum rate to the normal rate for the iron alone) is independent of the acid concentration and temperature.
- 4. The extent of promotion is much greater for ferric sulfate than for ferric chloride, although the maximum rate obtained in each case is the same. The promotion factors for the two systems approach each other as the concentration of iron approaches zero.
- 5. The facts are best explained by the following assumptions regarding the mechanism of promotion. (a) The iron salt is the primary catalyst, by virtue of its ability to form an intermediate compound. (b) The copper salt is a secondary catalyst, accelerating both the formation and subsequent decomposition of the intermediate product. The effect of the secondary catalyst is dependent upon its concentration only for very small quantities, a maximum effective concentration being noticeable. The mechanism of this secondary catalysis has not yet been completely explained.

Madison, Wisconsin

[Contribution from the Chemical Laboratories, Columbia University, No. 420]
FERRIC SALT AS THE "SOLUTION LINK" IN THE STABILITY
OF FERRIC OXIDE HYDROSOL¹

By Arthur W. Thomas and Alexander Frieden Received June 13, 1923

Ferric oxide hydrosol was first prepared by Arnold Maus.² It was regarded as a chemical compound³ until the introduction of the process of dialysis. Péan de St. Gilles⁴ and Thomas Graham⁵ looked upon it as

- ¹ This work was completed in February, 1922, and is adapted from the dissertation submitted by Alexander Frieden in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1922.
 - ² Maus, Ann. Phys. Chem., 11, 75 (1827).
- ³ Souberain, Ann. chim. phys., 44, 325 (1830). Rose, Ann. Phys. Chem., 24, 301 (1832). Schönbein, ibid., 39, 141 (1836). Scherer, ibid., 44, 453 (1838). Berzelius, "Lehrbuch der Chemie," 1845, vol. III, p. 555.
 - 4 Péan de St. Gilles, J. prakt. Chem., [1] 66, 137 (1855).
 - ⁵ Graham, Phil. Trans., 161, 183 (1861).

a soluble form of ferric hydroxide containing "impurities" but it soon became apparent⁶ that at least some of the impurities associated with this modification of hydrated ferric oxide were necessary for its stability in solution, as was found in the case of diverse colloidal dispersions, resulting in the evolution of the complex theory of colloids.⁷

Numerous attempts have been made to determine the relationship of the adsorbed electrolyte to the adsorbent, ferric oxide.⁸ Of these, the work of Linder and Picton,⁹ Malfitano,¹⁰ and Nicolardot¹¹ are important, though of little quantitative significance in the light of improved methods of investigation available at the present time. Interesting quantitative relationships have been obtained by Neidle,¹² by Pauli and Matula¹³ and, since the completion of this work, by Mathews and Browne,¹⁴ and by Browne,¹⁵

The object of this research was to obtain quantitative relationships between the substances that make up the colloidal particles and to determine the amount of electrolyte required to keep the particles dispersed.

Method

Preparation of the Hydrosols.—(1) About 14 M ammonium hydroxide solution was delivered drop by drop from a buret into a 3 M solution of ferric chloride, which was continually and vigorously agitated by a motor stirrer. The addition of ammonium hydroxide solution was continued until the resultant precipitate was peptized with great difficulty.

- (2) Ammonium hydroxide was added as above until a permanent precipitate was just formed; 0.33 *M* ferric chloride solution was then added, and the mixture stirred until the precipitate dispersed.
- (3) To a hydrosol prepared by Method 1 ferric chloride solution was added until the entire sol precipitated, and the resulting precipitate was dispersed in distilled water.
- (4) Fifty cc. of M hydrochloric acid was added to a freshly prepared and washed precipitate of ferric hydroxide prepared from 250 cc. of 3 M ferric chloride solution. The mixture was allowed to stand until the precipitate was peptized.

⁶ Kastner, Ann. chim. phys., [3] 57, 231 (1859). Debray, Compt. rend., 59, 174 (1864). Magnier de la Source, ibid., 90, 1352 (1880). Wiedemann, Ann. Phys. Chem., [3] 5, 45 (1878). Wagner, Kolloid Z., 14, 149 (1914). Wyrouboff, Ann. chim. phys., 7, 449 (1905). Hantz and Desch, Ann. Chem., 323, 38 (1902). Ruer, Z. anorg. allgem. Chem., 43, 85 (1905).

⁷ von Weimarn, "Zur Lehre der Zustande der Materie," Theodor Steinkopff, Leipzig, 1914, vol. 1, p. 60. Beans and Eastlack, This Journal, 37, 2667 (1915).

⁸ Krecke, J. prakt. Chem., [2] 3, 286 (1871).

⁹ Linder and Picton, J. Chem. Soc., 87, 1919 (1905).

¹⁰ Malfitano, Compt. rend., 139, 1221 (1904); 140, 1245 (1905); 141, 660, 680 (1905); 143, 172, 1141 (1906); Z. physik. Chem., 68, 232 (1909).

¹¹ Nicolardot, Ann. chim. phys., 6, 334 (1905); Compt. rend., 140, 310 (1905).

¹² Neidle, This Journal, 39, 2334 (1917).

¹³ Pauli and Matula, Kolloid Z., 21, 49 (1917).

¹⁴ Mathews and Browne, This Journal, 43, 2336 (1921).

¹⁵ Browne, ibid., 45, 297 (1923).

The hydrosols prepared by the first two methods were blood-red and perfectly clear to reflected and transmitted light. Those prepared by the third method were clear to transmitted, but slightly turbid to reflected light, while the sols prepared by the last method were decidedly turbid to reflected, although clear to transmitted light.

Dialysis.—Cups¹⁶ of very fine, unglazed porcelain were first tried as dialyzers. It was found, however, that these were permeable to ferric ions for only a short time. After a few days of dialysis, there was but a slight amount of ferric ion in the diffusate, though the hydrosol in the cup contained a large amount of ferric chloride. Evidently the membrane of ferric oxide formed within the walls of the cup is impermeable to ferric ion.

Unglazed porcelain cups could not, therefore, be used at this stage of dialysis. In subsequent dialysis experiments, in which all of the unadsorbed ferric chloride had left the solution and further dialysis was merely a slow hydrolysis, porcelain cups of smaller size and thinner wall were employed. These were permeable to chloride and hydrogen ions.

For the preliminary dialysis, collodion bags were employed. These bags were prepared in a 2-liter Florence flask and were changed as soon as a coating of ferric oxide had been formed on the walls of the membrane, in order to speed up the process of dialysis. Some of these sols were dialyzed at room temperature and others at 60°. The diffusate was changed every 24 hours, distilled water being used throughout. The preliminary dialysis was considered complete when the diffusate of 24 hours, usually 1 liter in volume, acidified and evaporated to 10 cc., showed no color upon addition of 5 cc. of M ammonium thiocyanate solution. In view of the high delicacy of this test for the ferric ion, its concentration in the hydrosol is negligible at this point. (The ratio 17 of the concentration in moles of ferric oxide to that of ferric chloride, Fe₂O₃/FeCl₃, was about ten at this point.) The test for the ferric ion as given by ammonium thiocyanate applied to the sol directly was negative long before this ratio was reached. The ammonium chloride formed in the preparation of the sol disappeared within a comparatively short time.

The length of time required for the completion of dialysis varied from 2 to 5 months, depending upon the concentration of the sol and the temperature at which the dialysis was performed. Excessive dilution of the dialyzing hydrosol was avoided by having the level of the water in the outer vessel much lower than that of the hydrosol inside.

¹⁶ Obtained from Coors Porcelain Company, Golden, Colorado.

¹⁷ The values given throughout this paper were obtained as follows. The chlorine found by analysis was calculated to ferric chloride; the ferric chloride computed to ferric oxide which was subtracted from the total ferric oxide (from total iron found by analysis), giving the values of ferric oxide cited.

Analyses

Iron.—The solution was evaporated with sulfuric acid until fumes of sulfur trioxide formed and was then reduced in a Jones reductor and was determined by titration with potassium permanganate.

Chlorine.—To a definite volume of the hydrosol, nitric acid was added to make the final concentration about 3 M. The covered beaker was allowed to stand in the dark until all of the ferric oxide had dissolved, which usually required a week or 10 days. Approximately 0.1 M silver nitrate was then added in excess of the amount necessary to precipitate all the chloride. A slight variation in the procedure was to add the silver nitrate before the addition of nitric acid. Separate experiments on pure potassium chloride showed that the procedures could be used interchangeably, and that there was no danger of loss of chloride by oxidation. The chloride concentration was determined either gravimetrically or by the method of Volhard.

Experimental Part

At the beginning of this investigation, measurements of the conductivity of ferric oxide hydrosol during dialysis were made in the hope of getting quantitative indication of an end-point in the purification. The measurements showed, as anticipated, that the conductivity gradually decreases as dialysis proceeds, but after a certain time the hydrosol showed a conductivity lower than that of the distilled water against which it was being dialyzed. The conductivity of ferric oxide hydrosol has been reported by several investigators, 10,13,18 but the results differ widely because of the variable quantities of peptizing electrolyte present and are obviously of no value.

Due to the failure of the conductivity method, the measurement of the depression of the freezing point was tried, and since this also failed to serve our purpose (see later), the observation of beginning of precipitation was adopted as end-point in dialysis. The incipience of precipitation does not mean the coagulation of the hydrosol, since thereafter precipitation proceeds gradually, the system assuming a turbid appearance which increases with continued dialysis until finally the entire sol becomes a gel.

Two and one-half liters of a sol (Fe₂O₃, 9.3105; FeCl₃ 0.7143 g./liter; ratio, 13) was dialyzed for 4 weeks at room temperature against a volume of 1 liter of distilled water, the outside water being changed several times each day for the first week and once a day thereafter. Samples were withdrawn for analysis at frequent intervals until precipitation began. At this point the hydrosol contained 3.2653 g./liter of ferric oxide and 0.1539 g./liter of ferric chloride, that is, a molar ratio, Fe₂O₃/FeCl₃, of

¹⁸ Duclaux, Compt. rend., 140, 1468 (1905); Kolloid Z., 3, 126 (1908). Goodwin and Graver, Phys. Rev., 9, 251 (1896); 11, 193 (1900). Dumanski, Z. physik. Chem., 60, 553 (1907).

21.5. The dialysis was continued for 10 weeks, until all of the sol was converted to a gel in which the molar ratio of ferric oxide to ferric chloride was 48.

A sol was dialyzed at 60° for 10 weeks. At the end of this time, the 24-hour diffusate when evaporated to 10 cc. gave no test for ferric ion. The sol then contained 8.1017 g./liter of ferric oxide and 0.8397 g./liter of ferric chloride. When precipitation began (after 18 days) the hydrosol contained 1.1961 g./liter of oxide and 0.0593 g./liter of chloride thus showing a molar ratio of 20.5.

This would seem to indicate that dilution has no marked effect on the point at which precipitation begins.¹⁹ To verify this, two sols of molar ratios 11.7 and 12.9 were made up to various dilutions and dialyzed in collodion bags to the first appearance of a precipitate. The two series showed identical results, the first of which is described in Table I.

TABLE I

EFFECT OF DILUTION ON END-FORT								
Dilution	none	1.87	3.04	7.75	13.80			
Fe ₂ O ₃ , g./1	4.1838	2.3144	1.3711	0.5396	0.3019			
FeCl ₃ , g./1	0.3637	0.1118	0.0650	.0266	.0149			
Ratio of Fe ₂ O ₃ to FeCl ₃	12^{a}	21	22	21	21			

^a Original sol. not dialyzed to incipience of precipitation.

It was deemed probable that the gradual precipitation, which sets in after the initial appearance of precipitate, might be due to excessive hydrolysis and dialysis near the walls of the collodion bags. If so, this would affect the limiting ratio. To test this probability, a series of sols was dialyzed in small, unglazed porcelain cups. The solutions were stirred throughout the entire period by a current of nitrogen, kept at a temperature of 50–60°, and analyzed when a turbidity became perceptible.

The data in Table II are taken from one of two series of different sols which gave identical results. The sol used in Table II contained 5.867 g./liter, of ferric oxide and 0.3743 g./liter, of ferric chloride; ratio = 16.

TABLE II
EFFECT OF DILLITION ON END-POINT

Dilution	none	1.33	2.00	2.66	4.00		
Fe ₂ O ₃ , g./1	4.9186	3.6492	2.3434	1.6119	1.4292		
FeCl ₃ , g./1	0.2453	0.1829	0.1160	0.0934	0.0669		
Ratio of Fe ₂ O ₃ to FeCl ₃	20	20	21	20	22		

Following the incipience of precipitation, gradual flocculation was observed in all cases. Analyses of samples of such sols showed that their molar ratios of ferric oxide to ferric chloride gradually increased as dialysis

¹⁹ The value at which incipience of precipitation is found and the fact that dilution of the sol does not affect it are not in agreement with the experience of Neidle, Ref. 12.

continued to final complete precipitation. These analyses were not very accurate because it was impossible to free the hydrosol entirely from precipitated particles that were held in suspension. Centrifuging at about 1000 "times gravity" for the purpose of removing these suspended particles frequently resulted in the breaking out of the entire dispersed phase from dispersion in the form of a fairly continuous jelly phase. This is rather significant in that it suggests a jelly-like structure of this hydrosol. Due to the inaccuracies of the analyses the results are not reported, but it is of interest to recall that Duclaux²⁰ claimed that ferric oxide hydrosol could be dialyzed to a limiting value of 170 Fe₂O₃. 1FeCl₃.

Since the dispersed phases of hydrosols, prepared as just described, migrate to the cathode when subjected to the action of an electrical current, the particles are said to be positively charged due to the ferric chloride of the complex, the ferric ions thereof remaining in contact with the ferric oxide while the chloride ions are located in the water phase directly bathing the particles. Since like charged bodies repel one another, the electrical charges of the particles are supposed to overcome the mutual attractive forces of the particles, a rather commonly accepted explanation for the stability of inorganic colloidal particles.

According to this explanation, the limiting ratio of ferric chloride to ferric oxide should increase with increased concentration of the particles, since the mutual attractive force varies inversely as some power of the distance between the particles. The more closely the particles are packed, the greater should be the charge required to keep them repelling one another.

Examination of the data reveals no such tendency. Apparently the electrical charge is not the predominating factor for the stability.²¹ The

In his famous paper on the "Mathematical Theory of the Kinetics of the Coagulation of Colloidal Solutions," M. v. Smoluchowski [Z. physik. Chem., 92, 129 (1917)] arrives at conclusions identical with the statements of Professor Porter quoted above.

²⁰ Duclaux, Compt. rend., 143, 296 (1906).

²¹ In connection with this statement it is timely to quote the criticism of the electrical charge theory of stability recently made by Porter and Hedges [Phil. Mag., 44, 641 (1922)]: "If the particles really contained charges all of one sign only they would tend to move toward the boundary. This is the equivalent of the fundamental electrical fact that statical charges reside close to the surface of conductors. When we are dealing with large particles instead of electrons, there is no doubt that they would occupy a larger region, instead of a thin superficial area, but still there would be an accumulation at the boundary. This is the opposite to what is observed." "But the charges in the solution are not only of one sign. The solution, as a whole, is uncharged; consequently an equal opposite charge is to be looked for. This opposite charge is the second member of the double layer close to the surface of each particle. When the existence of this double layer is recognized, the electric forces between the particles become zero, except insofar as relative displacement takes place by induction between two members of a layer so as to give it an electrical movement. In this case the force between two such doublets in the equilibrium state will, on the average, be an attraction and not a repulsion."

fact that the limiting ratio, that is, the point corresponding to incipience of precipitation, is always nearly the same²² indicates that regardless of the concentration of the sol, 1 mole of ferric chloride is required to keep about 21 moles of ferric oxide dispersed in the colloidal condition.²³ Any amount of ferric chloride in excess of this ratio might be regarded as impurity. The stability of the ferric oxide hydrosol must then be due not to the electrical charge of the particles but to the solution forces (solubility) of the adsorbed ferric chloride. The high solution forces of the ferric chloride molecules pull the ferric oxide particles with which they are combined by secondary valence or "adsorption forces" into semisolution. Upon removal of the ferric chloride by hydrolysis the insoluble particles of ferric oxide, having lost their "solution-link," precipitate.

According to the "solution-link" hypothesis this hydrosol should be soluble in any liquid in which ferric chloride dissolves. It was found that dilution of the hydrosol with an unlimited amount of alcohol had no effect upon its appearance, nor did the addition of ether to this alcosol precipitate it, provided a large excess was not added.

An iron oxide hydrosol stabilized by ferric sulfate should be precipitated by alcohol according to the hypothesis. Such a sol was prepared resembling the Péan de St. Gilles sol in appearance. Addition of alcohol precipitated it instantly.

Hydrogen-Ion Concentration.—Pauli and Matula¹³ attempted to measure the hydrogen-ion concentration of ferric oxide hydrosols. Good results were obtained by them when using sols which had "aged" for 6 months or which were heated for a few hours at 80°, this being equivalent to aging, that is, hydrolyzing excess ferric chloride. Their measurements had to be made quickly and their platinum electrodes were saturated with hydrogen before coming in contact with the hydrosol to be measured. The results indicated that the hydrosols were neutral,²⁴ that is, had a hydrogen-ion concentration of the order of 10⁻⁷.

Measurements of hydrogen-ion concentration would be impossible in the presence of ferric ion for obvious reasons. Using well dialyzed sols in which the concentration of ferric ions was supposedly nil, we found no evidence of a reducing potential but could not get what is considered to be an absolutely satisfactory equilibrium reading due to the deposition of ferric oxide gel upon the platinized electrode. However, taking the mean of a series of readings which were not widely divergent, a hydrogen-

 $^{^{22}}$ The slight deviations from the value of 21 may be ascribed as due to errors in the determination of the end-point of dialysis by means of the observation of the beginning of precipitation.

²³ This is the "purity" at which Browne (Ref. 15) found the heat of coagulation of ferric oxide hydrosol to be practically zero.

²⁴ Very recently, Browne (Ref. 15) using a similar method also reports that ferric oxide hydrosols are neutral.

ion concentration of $10^{-4.9}$ was indicated. This was the same for a series of our "pure" hydrosols of various concentrations and consequently the hydrogen-ion concentration does not appear to depend upon the concentration of the dispersed phase, at least over the range which we studied. We should say that our "pure" ferric oxide hydrosols showed a hydrogenion concentration of 10^{-5} .

An acid reaction is to be expected, since upon dialysis of sols from which the free ferric chloride has been removed only hydrogen and chloride ions are found in the diffusate across the collodion membrane. Consequently, the ferric chloride of the dispersed phase is in equilibrium with the ions of hydrochloric acid in the dispersion medium, which in the case of our "pure" sols is of the order of $0.00001\ M_{\odot}$.

Behavior upon Freezing.—As previously mentioned, freezing-point depression was tried as a quantitative method for following purification, but it was found that a well dialyzed sol gives a depression of the freezing point within the range of experimental error of measurement with the Beckmann thermometer.

Péan de St. Gilles was inclined to regard his hydrosols as true solutions because they froze in a "normal" manner. In 1889, Ljubawin²⁶ froze, among other colloidal substances, ferric oxide hydrosol and found that as the liquid cooled, particles of ferric oxide concentrated in the center while the periferous layers of the ice became colorless. When the mass was melted again, all of the iron oxide particles redispersed. Lottermoser²⁶ found that only those sols which are deficient in electrolyte were precipitated on freezing. Sols rich in electrolyte were not affected even upon continued freezing.

Our experiments showed that when a pure ferric oxide hydrosol is only partially frozen, ice crystals are formed which upon melting leave the sol as homogeneous in appearance as it was before the operation. But when cooling is continued until freezing is complete, some precipitation is noted when the mass melts. The longer the sol has been cooled, the greater will be the amount of gel formed. The precipitate is in the form of short, amorphous, shiny, needle-like particles. When the sol is allowed to remain in contact with the ice-salt mixture for some length of time, the entire solution turns to a dark red, solid mass. When cooling is continued separation of the water begins as a layer of colorless ice near the walls of the test-tube, and such layers continue inward until, in the center, there are deposited the red brown particles above described. These particles are arranged in a string-like formation throughout the height of the tube. When the ice is melted they do not redisperse. The water obtained by melting the ice shows a barely perceptible test for chloride ion and none

²⁵ Ljubawin, Z. physik. Chem., 4, 486 (1889).

²⁸ Lottermoser, Ber., 41, 3976 (1908).

for ferric ion. The gel particles are practically insoluble in dil. nitric acid, but readily soluble in concentrated acid. Analysis showed that about 80% of the ferric chloride of the original hydrosol particles was retained in this gel. This behavior is quite different from that of Bredig gold hydrosols upon freezing, since Beans and Beaver²⁷ find that all of the stabilizing electrolyte is removed from the gold particles through the congelation.

These observations support the conclusion that the stability of these hydrosols is due to the solution forces of the adsorbed ferric chloride rather than to the electrical charge of the particles.

The ferric chloride in the congelation gel from the pure sols must be dispersed throughout the compact solid mass, for although there is sufficient ferric chloride present to redisperse the particles, at least partially, such redispersion does not take place; but when an impure sol is frozen, that is, one to which some ferric chloride has been added, the gel particles redisperse upon melting; this is like the experience of Gutbier and Flury²⁸ with selenium oxide sols.

Relationship Between Graham's Hydrosol and the So-Called "Meta-iron" Hydrosol of Péan de St. Gilles. Water of Hydration.—The hydrosol that Péan de St. Gilles prepared by heating and boiling solutions of the acetate differed slightly in properties from Graham's in that it was not so clear and that a precipitate formed on continued heating which was insoluble in concd. acids but soluble in dil. acids and water. Graham, in analogy to the two modifications of tin oxide sol, called it the "meta-iron" oxide hydrosol, an appellation that is still used.

In the course of this investigation, it was found that this conception of two modifications of ferric oxide hydrosol is not justifiable, the main difference between the two being water of hydration of the particles, as suggested by others.^{29,30}

This was demonstrated as follows. A hydrosol prepared by Method 3 was dialyzed at room temperature until it showed the molar ratio, Fe₂O₃/-FeCl₃ = 18. A portion of this sol was then dialyzed in a porcelain cup at about 60° while it was continuously stirred with nitrogen and was analyzed (a), after 5 days of dialysis, and then again (b) after 9 days. In (a) incipience of precipitation was not evident while in (b) a decided precipitation had started. The ratios of Fe₂O₃/FeCl₃ were (a) 20 and (b) 26. Another hydrosol prepared by peptizing ferric hydroxide gel with a small amount of hydrochloric acid was dialyzed as described above. This initially turbid sol increased in turbidity as dialysis was continued so that

²⁷ D. J. Beaver, Dissertation, Columbia University, 1921.

²⁸ Gutbier and Flury, Kolloid Z., 29, 161 (1921).

²⁹ Roscoe and Schorlemmer, "Treatise on Chemistry," D. Appleton and Co., 1900, vol. 2, p. 998.

³⁰ Bancroft, J. Phys. Chem., 19, 232 (1915).

the beginning of precipitation could not be determined accurately. When the end-point was presumed to have been reached, it showed upon analysis a ratio, $Fe_2O_3/FeCl_3 = 23$.

It is thus seen that the limiting value for these "meta-iron oxide," or Péan de St. Gilles' sols is of the same magnitude as that of the Graham sol. This would indicate that the turbidity of this sol is due to dehydration rather than to the presence of larger ferric oxide aggregates.

Since, according to Einstein,³¹ the viscosity of a colloidal dispersion is expressed by the formula $\eta' = \eta(1+kf)$, where η' is the viscosity of the system, η the viscosity of the dispersion medium, and f the ratio of the total volume of the dispersed phase over the total volume of the system, which means as Wo. Ostwald³² and others have shown that the viscosity of a colloidal solution increases with the amount of the dispersion medium taken up by the dispersed phase, the Péan de St. Gilles sol should have a lower viscosity than the Graham sol of the same concentration if our supposition is correct.

To determine whether this is the case, 10cc portions of a Graham hydrosol were treated with various amounts of 2N ferric chloride solution until the turbidity which first appeared gradually changed to a coarse bright yellow dispersion³³ and the viscosities were measured.

The measurements were made by means of an Ostwald viscometer, in a constant temperature bath at $25 \pm 0.01^{\circ}$. Table III shows the results. The figures signify the time in seconds for outflow.

Table III Viscosity of Graham Hydrosol, No. 15

FeCl ₃ Expt.	added Cc.	Time. Sec.	Comparative data	Time Sec.
2	0.1	73	Pure hydrosol (Expt. 1)	81
3	0.2	73	Distilled water	71
4	0.3	74	10 cc. dist. water + 2 cc. of 2 N FeCl ₃	-80
5	0.5	75	10 cc. dist. water + 10 cc. of 2 N FeCl ₃	137
6	1.0	78		
7	2.0	99		

No. 1 was perfectly clear; Nos. 2, 3, 4 and 5 were clear to transmitted, but turbid to reflected light. They resembled the Péan de St. Gilles sol in all respects. The turbidity gradually increased with increasing amounts of ferric chloride. No. 6 was decidedly brown while No. 7 was yellow. After three hours, the viscosities were again measured and found to be unchanged.

From these results it is seen that the addition of ferric chloride first decreases the viscosity and then increases it. The decrease in viscosity

³¹ Hatschek, Kolloid Z., 7, 301 (1910); 8, 34 (1911).

³² Wo. Ostwald, Trans. Faraday Soc., 9, 34 (1913).

³³ A sol so treated is identical in appearance with the "meta-iron oxide" modification.

indicates a diminution in size of the particles which could only have been caused by a loss of water of hydration by the dispersed phase. The increase in viscosity observed upon the addition of larger amounts of ferric chloride is due to the coalescence of the particles preliminary to precipitation.

As to the mechanism of the dehydration of the sol by ferric chloride, we can only venture to say that it is possibly due to the high hydration of the electrolyte added, thus causing a partial dehydration of the dispersed Fe₂O₃–FeCl₃–H₂O phase, or in view of the fact that this sol migrates in an electrical field showing that the adsorbed and peptizing electrolyte is ionized, even though the degree be extremely small, then the Donnan effect of the added ferric chloride would result in a decrease in swelling (hydration) of the dispersed phase as in the case of the addition of hydrochloric acid or a neutral salt to gelatin jelly swollen in a solution of hydrochloric acid. Both suggested mechanisms may operate at the same time.

Summary

Evidence is submitted which indicates that the stability of ferric oxide sol, stabilized by ferric chloride, is due to the solubility (or solution forces) of the adsorbed ferric chloride in the dispersion medium, rather than to the mutual repulsive forces of the particles presumed to reside in their electrical charges of like sign. The so-called "meta-iron" sol of Péan de St. Gilles is one in which the particles of the dispersed phase are less hydrated than in the Graham ferric oxide hydrosol.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY, No. 421]

THE MECHANISM OF THE MUTUAL PRECIPITATION OF CERTAIN HYDROSOLS¹

By Arthur W. Thomas and Lucille Johnson Received June 13, 1923

The literature² concerning the mutual precipitation of hydrosols treats this phenomenon as an electrical one by which the positively charged particles of one hydrosol neutralize the negatively charged particles of the

- ¹ Adapted from the dissertation submitted by Lucille Johnson in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York City, May, 1923.
- ² Linder and Picton, J. Chem. Soc., 71, 586 (1897). Lottermoser, "Anorg. Kolloide," Stuttgart, 1901, p. 77; through Zsigmondy-Spear, "Chemistry of Colloids," Wiley and Sons, New York, 1917, p. 56. Bechhold, Z. physik. Chem., 48, 385 (1904). Neisser and Friedman, Münch. Med. Wochschr., 51, 465, 827 (1904). Henri, Compt. rend. soc. biol., 55, 1666 (1903). Teague and Buxton, Z. physik. Chem., 60, 489 (1907). Spring, Bull. acad. roy. Belg. (Sciences), 1900, p. 483. Biltz, Ber., 37, 1095 (1904). Billitzer, Z. physik. Chem., 51, 129 (1905).

other, but the recent discovery by Freundlich and Nathansohn³ showing that arsenious sulfide hydrosol and sulfur (Odén) hydrosol precipitate each other, although both are "negatively charged," is not amenable to explanation by this hypothesis. A satisfactory chemical explanation is available, however.

A short paper by Lottermoser⁴ in 1910 suggested a chemical mechanism for mutual precipitation of colloids which was based upon a few experiments with silver iodide hydrosol peptized by silver nitrate (or by silver ion) and silver iodide sol peptized by potassium iodide (or the iodide ion). He found sharpest and most complete mutual precipitation in those mixtures where the amounts of peptizing silver nitrate and potassium iodide were in, or very near, chemical equivalence.

In the belief that mutual precipitations of colloids are chemical phenomena this investigation was undertaken. A series of "positively charged" ferric oxide hydrosols was treated with a number of "negatively charged" silicic oxide hydrosols and the precipitation quantitatively studied from the contents of peptizing electrolyte. The reaction between ferric oxide sols and arsenious sulfide sols was followed qualitatively.

Preparation and Analysis of Ferric Oxide Sols

Preparation.—Ferric oxide sols were prepared by adding $2\,M$ ammonium hydroxide very slowly, by dropping from a buret, to $2\,M$ ferric chloride solution which was vigorously stirred until the precipitated ferric hydroxide ceased to peptize or "dissolve" easily. The sols, which were very dark in color, were dialyzed in collodion bags against distilled water until the desired degree of "purity" was reached.

Analysis.—Iron. Three cc. of concd. sulfuric acid was added to 25 cc. of sol and the solution evaporated to dryness on a hot-plate. This was to insure removal of chlorine. The dried residue was dissolved in 150 cc. of water, 10 cc. of 18 M sulfuric acid added, the solution passed through a Jones reductor and titrated with standard potassium permanganate. Correction was made for the reducing of a blank of sulfuric acid.

Chlorine by Volhard's Method.—Ten cc. of nitric acid prepared by diluting concd. acid (d., 1.42), from which all oxides had been removed, with an equal volume of water, was added to 50 cc. of the sol and the mixture allowed to stand in a dark, cool place until the solution was clear. An excess of standard 0.1 M silver nitrate solution was added, the silver chloride filtered off and the excess titrated with 0.1 M potassium thiocyanate solution using the iron as indicator.

TABLE I
Composition of Ferric Oxide Sols

No.	Moles FeCla	Moles Fe ₂ O.	Fe ₂ O /FeCl ₂	No.	Moles FeCla	Moles Fe ₂ O ₃	Fe ₂ O ₃ /FeCl ₃
1	0.00895	0.0482	5 35/1	15	0.00518	0.0507	9.8/1
2	.01075	.0509	4.8/1	17	.00267	.0346	13./1
3	.00889	.0483	5.37/1	20	.00145	,0267	18.5/1
4	.00338	.0294	8.65/1	21	.00230	.0367	15.9/1
6	.00178	.0191	10.6/1	23	.00238	.0339	14.3/1

³ Freundlich and Nathansohn, Kolloid Z., 28, 258 (1921); 29, 16 (1921).

⁴ Lottermoser, Kolloid Z., 6, 78 (1910).

The amount of iron as iron chloride was calculated from the chlorine and this subtracted from the total iron gave the iron from which ferric oxide was calculated.

Silicic Acid Sols

Preparation.—Silicic acid sols were prepared by dissolving water glass (d., 1.4) in 10 times its weight of water and partially neutralizing to various degrees with hydrochloric acid. The sodium chloride formed was not removed because (1) the freshly prepared sols diffused quite readily through unglazed porcelain dialyzers and through ordinary collodion sacks; these sols after standing showed aggregation of particles (became opalescent) and then would not diffuse through the septa mentioned; but removal of sodium chloride by dialysis would also remove sodium hydroxide formed by hydrolysis of sodium silicate, which was not desired; (2) the presence of the sodium chloride did not complicate the results, as shown later.

Analysis.—Silicic Acid. To a portion of the sol was added several cubic centimeters of $12\ M$ hydrochloric acid and the mixture was evaporated to dryness. The residue was twice wet with hydrochloric acid and evaporated to dryness, after which it was washed free from chlorides and weighed as silicon dioxide.

Sodium Silicate.—A portion of the sol was diluted with four or five times its volume of water, making a total volume of 100 or 200 cc., depending on the concentration of the sol. Ten cc. of a concd. solution of sodium chloride was added to replace sodium hydroxide which might be held in the dispersed phase, and the solution titrated with $0.1\,M$ hydrochloric acid, using phenolphthalein as indicator. After neutrality was apparently reached the solution became pink upon standing, and a few drops of acid were necessary to discharge the color. To avoid errors due to this, a check was run by adding an excess of acid and titrating with sodium hydroxide; the results checked within 2%, which is well within the error of the subsequent determinations of precipitation ratios.

Sodium Chloride.—The sodium chloride was calculated from the amount of hydrochloric acid added to the water glass to form the silicic acid sol.

As no definite formula can be given for the sodium silicate, the concentrations are expressed in terms of silicon dioxide for silicic acid and sodium hydroxide for the stabilizing sodium silicate.

TABLE II
COMPOSITION OF SILICIC ACID SOLS
In moles per liter

No.	1	2	3	4	5
SiO ₂	0.221	0.208	0.305	0.437	0.186
NaOH	0.0327	0.0356	0.0294	0.135	0.0115
SiO ₂ : NaOH	6.7/1	5.8/1	10.4/1	3.5/1	1.6/1
NaCl	0.091	0.081	0.142	0.111	0.093

Procedure

Various amounts of one sol were run from a buret into hard glass, bacteriological tubes of uniform diameter and clearness and about 20 cc. in volume. Equal volumes of the other sol were run from a pipet or buret into the tube as quickly and as quietly as possible to avoid mixing. The tubes were inverted two or three times with as little agitation as possible, to insure complete mixing of the sols. This was sufficient if the tubes were not more than $^3/_4$ full and were revolved as they were inverted. The point of maximum precipitation could be clearly seen by successive stages; first, the greatest cloudiness in the series, followed by the first separation of par-

ticles, and usually the first sediment. The last was frequently over a wider range than the first two stages as the precipitating zone widened rapidly. All observations were made immediately after mixing by holding the series of tubes against a clean or open window. Artificial light was found to be quite unsatisfactory, as was the light late in the afternoon or on a dark day.

Some series precipitated more easily than others, probably because of greater agitation. Vigorous shaking usually precipitated the whole series immediately. A tube of greater diameter than the others or of cloudy or marked glass appeared more cloudy and consequently was misleading. A few series were centrifuged, but the time required in placing them in the centrifuge and the force to throw out the fine particles resulted in complete precipitation over a wide range.

To avoid errors due to an unclean tube or some other factor, three or four determinations were made in each instance.

The effect of dilution of the sols is given in Table III.

Table III

Effect of Dilution upon Mutual Precipitation
Cc. Precipitation Millimole

Ŧ	Cc. e ₂ O ₂ sol No. 6	Ce, SiO ₂ No. 1	Precipitation results	HCl Millir	noles NaOH
	(Dilution 1:				1,0024
	5.3	1 to 10	All coagulated to solid		
2.	(Dilution 1:	10 1:50)			
	5.3	3.0	Partial)		
	5.3	3.5	Almost complete (0.00004	a angen
	5.3	4.1	Complete	0.00284	0.00268
	5.3	4.5	Almost complete		
3.	(Dilution 1:	50 1:250)	,		
	5.3	4.5	Partial		
	5.3	4.8	Complete	0.00057	0.00004
	5.3	$5.1 \stackrel{?}{)} 4.9$	Complete	0.00007	0.00064
	5.3	5.4	Partial		
4.	(Dilution 1:	100 1:250)			
	10	4.7	Much slower		
	10	5.0	First to ppt.	o occar	0.00050
	10	5.3	Much slower	0.00065	0.00053
	10	5.6	Much slower		

This table shows that the dilution of mutually precipitating sols narrows and sharpens the zone of maximum precipitation, and that the variation in ratio between the sols varies no more than in successive experiments with the same dilution. If carried beyond certain dilutions coagulation is almost imperceptible or is so slow that it is very difficult to determine. The dilutions used for the work were the greatest giving sharp precipitations. Very unstable sols show considerably different ratios with dilution. This will be discussed later.

To avoid possible differences due to order of mixing, the order was always reversed at least once.

Table IV gives the data found in determining the points of maximum precipitation in cases typical of 37 experiments made, and Table V shows results obtained with one silica sol and several ferric oxide sols, which are typical of two other similar series.

TABLE IVA

MUTUAL PRECIPITATION OF SILICIC ACID HYDROSOL NO. 1 WITH FERRIC OXIDE HYDROSOL NO. 20

Dilutions: Fe_2O_3 sol = 1:25 SiO₂ sol = 1:200 5.3 cc. of ferric oxide sol added to silicic acid sol

First test		Second test		
Cc. SiO ₂ soI	Results	Ce. SiO ₂ sol	Results	
4:0	Partial precipitation	4.5	Partial later precipitation	
5.0	First and heaviest precipitate	5.0	The 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	
6.0	Partial precipitation	5.5∫	First to precipitate	
7.0	Only slightly cloudy	6.0	Partial later precipitation	

It was evident that 5.2 cc. of silicic acid sol with 5.3 cc. of ferric oxide sol gives the maximum precipitation.

TABLE IVB

Silicic acid sol added to 5.3 cc. of ferric oxide

Cc. SiO ₂ sol	Results	Cc. SiO2 sol	Results
4.8	Fourth to precipitate	5.4	Second to precipitate
5.0	Second to precipitate	5.6	Third to precipitate
5.2	First to precipitate		

Maximum precipitation is obtained with 5.2 cc. of silicic acid sol and 5.3 cc. of ferric oxide sol.

TABLE V

THE RATIO AT MAXIMUM PRECIPITATION OF SILICIC ACID SOL NO. 1 TO DIFFERENT FERRIC OXIDE SOLS

			aprette Carryay	POSTANI		
	Fe ₂ O ₃ sol		Milli-eqt	SiO2 sol		
No.	Dilution	Ce,	Chloride	Sodium	Ce.	Dilution
1	1:100	10.0	0.00199	0.00151	4.6	1:100
2	1:100	5.3	.00171	.00124	3.8	1:100
3	1:100	10.0	.00267	.00180	5.5	1:100
4	1:100	10.0	.00102	.00112	3.5	1:100
6	1:100	10.0	.00054	.00065	5.0	1:250
15	1:50	5.3	.00165	.00155	9.5	1:200
17	1:50	5.3	.00085	.00085	5.2	1:200
20	1:25	5.3	.00085	.00085	5.2	1:200
21	1:25	5.3	.00147	.00164	10.0	1:200
23	1:25	5.3	.00151	.00155	9.5	1:200

Silicic acid sol No. 4 was precipitated at different dilutions against ferric oxide sols Nos. 4, 6 and 20. No clear zones could be determined, but in every case the milli-equivalents of sodium exceeded the milli-equivalents of chloride.

The precipitating volumes checked within 10% in all cases except that of the very impure silicic acid sol No. 4.

To test the effect of the sodium chloride present upon the point of maximum precipitation 0.03 g. of sodium chloride (an amount equal to 60% of the amount of sodium chloride already present in the sol), was added to silicic acid sol No. 2 (diluted 1: 200), and the sol precipitated with several ferric oxide sols.

The results showed that the sodium chloride is without influence on the mutual precipitation of silicic acid sols and ferric oxide sols, and consequently no error was introduced by its presence in the silicic acid sols used.

TABLE VI

THE RATIO OF FERRIC CHLORIDE EXPRESSED IN EQUIVALENTS OF HYDROCHLORIC ACID
TO SODIUM SILICATE

Expressed in equivalents of sodium hydroxide in the thirty-seven precipitations of ferric oxide sol and silicic acid cited in the foregoing tables. The values are milli-equivalents of sodium hydroxide per 0.001 milli-equivalents of hydrochloric acid.

The soland since acid creed in the following teaches. The values are infine-equivalents of sodium hydroxide per 0.001 milli-equivalents of hydrochloric acid.

The sols are arranged in the order of their purity, the ratio of sodium silicate in terms of sodium hydroxide to silicon dioxide decreasing from left to right, and the ratio of ferric chloride to ferric oxide decreasing from top to bottom

			Silicie Acid	Sols		
1	Number	4	2	1	3	5
Mole	s NaOH/SiO ₂	1/3.5	1/5.8	1/6.7	1/10.4	1/16.1
-Feri	ric oxide sols— Moles					
No.	FeCl ₃ /Fe ₂ O ₃					
2	1/4.8		0.00061	0.00073	0.00080	
1	1/ 5.35		.00080	.00055	.00077	
3	1/5.37		.00073	.00069	.00077	
4	1/8.65	>100%	.00096	.00091	.00090	
15	1/9.8		.00090	.00100	.00080	0.00029
6	1/10.6	>100%	.00106	.00094	.00082	
17	1/13		.00101	.00090	.00080	.00043
23	1/14.3		.00101	.00091	.00090	.00048
21	1/15.9	>100%	.00098	.00110	.00080	.00044
20	1/18.5		.00093	.00100	.00080	
Av. (Excl. of 2, 1, 3)	>100%	.00098	.00095	.00083	.00041

Table VI shows that over a wide range of ratios between peptizing agent and dispersed phases of sols, there is a constant ratio between the peptizing agents of mutually precipitating sols and a greatly varying ratio between the dispersed phases. This leads to the conclusion that the precipitation is due to removal of the peptizing agents by a chemical action between them. As no definite formula can be given for the silicates it is impossible to express the reaction between sodium silicate and ferric chloride in an equation. However, the peptizing ferric chloride and sodium silicate can be given in terms of their hydrolysis products which are in equilibrium with the dispersed phase complexes, and consequently in the mutual precipitation of ferric oxide and silicic acid sols the reaction may be expressed as $HCl + NaOH \longrightarrow NaCl + H_2O$.

Another indication of such a reaction is given by the difference of hydrogen-ion concentration in the supernatant liquid of precipitation of varying degrees. Various amounts of silicic acid sol No. 3 (diluted 1:25) were added to 25 cc. of ferric oxide sol No. 4 (diluted 1:10), the precipitates allowed to settle and the hydrogen-ion concentrations of the supernatant liquids determined with the results given in Table VII. The ferric oxide sol showed a Sörensen value (Ph) of 5 while the silicic oxide sol was slightly alkaline to phenolphthalein.

Table VII
Change in Hydrogen-ion Concentration with Varying Precipitation of Ferric
Oxide and Silicic Acid Sols

Silicic acid Cc.	l sol Remark		Tegative log on concentration	1
10	Very slig	ht pptn.	5.6	
	Excess of	f Fe ₂ O ₃ sol		
16	Maximu	m pptn.	6.8	
18	2nd of se	ries to ppt.	7.8	
20	Slow potn. Ex	cess of SiO ₂ sol	>8.3 (Alkalia	ne to phenolphthalein)

Thus it is evident that maximum precipitation occurs at neutrality as the chemical equivalence of peptizing electrolyte demands and that the acidity increases with excess ferric oxide sol, and the alkalinity increases with an excess of silicic acid sol.

The ferric oxide sols, excluding Nos. 1, 2 and 3 (which contain the greatest amount of the peptizing agent in proportion to the dispersed phase), give a 1:1 ratio with silicic acid sols Nos. 1 and 2. With silicic acid sol No. 3, the same ferric oxide sols give a constant ratio with the ferric chloride of the same ferric oxide sols. As the sol becomes purer in respect to peptizing agent, it becomes more unstable and the precipitating ratios become more inconstant. This agrees with the general experience with "pure" ferric oxide sols. It is known that when a certain degree of "purity" is passed in a sol, the sol precipitates. The sol containing only a little more than the necessary minimum of peptizing agent is in a metastable condition, and the least disturbance will precipitate it. This may easily account for the ready precipitation of the pure ferric oxide sols.

The effect of diluting unstable sols in mutual precipitation is shown in Table VIII.

TABLE VIII

Precipitation of Ferric Oxide Sol No. 17 with Silicic Acid Sol No. 5 of Various Dilutions

Fe ₂ O ₃ sol, 1:50 M	illi-equivalen	ts of HCl, 0.00160	
SiO ₂ sol	1:50	1:100	1:200
NaOH, milli-eq	0.00057	0.00069	0.00080
NaOH eq. of HCl eq. %	35	. 43	50

Thus it is seen that the reaction between very "pure" sols tends to approach chemical equivalence upon dilution, which is to be expected since

the individual particles becoming widely separated upon dilution have less chance of aggregating and thus settling out. In the mean time there is more chance for a complete reaction between the peptizing agents.

Both ferric oxide and silicic acid sols show erratic results in precipitation, if they contain large amounts of peptizing agent. This is undoubtedly due to the fact that some of the unaffected peptizing agent is adsorbed in the coagulum and carried down with it.

Investigation of the Mutual Precipitation of Ferric Oxide and Arsenic Trisulfide Sols

The ferric oxide sols used in this work were the same as those used with silicic acid sols and the method of procedure was the same.

Arsenic Trisulfide Sols

Preparation.—Hydrogen sulfide was passed into a warm solution of arsenic trioxide prepared by dissolving from 5 to 10 g. of finely powdered resublimed arsenic trioxide in a liter of boiling water that had been boiled first to remove dissolved oxygen.

Analysis.—Attempts were made to drive over the excess hydrogen sulfide and thus determine it directly, but in every instance there was decomposition of the arsenic trisulfide. For example, 100 cc. of sol containing only 1 cc. of phosphoric acid (d., 1.7) was completely dissolved by 15 minutes' boiling. This was surprising in view of the generally accepted ideas of the stability of arsenic trisulfide, and may be due to its fine subdivision in the sol. At no time was there precipitation during the heating, unless electrolytes had been added to the point of precipitation.

Ward⁵ states that at temperatures below 35°, the adsorbed hydrogen sulfide can be evolved from arsenic sulfide without decomposition of the latter, but several attempts to remove only the hydrogen sulfide by passing carbon dioxide gas through the pure sol, or through the sol previously precipitated by neutral salts, resulted in appreciable decomposition and this technique was thereby proved valueless.

Freshly prepared sols were analyzed for total arsenic and sulfur. From the arsenic percentage, the amount of trisulfide present was calculated and the sulfur found in excess of that to give this amount was calculated as hydrogen sulfide of peptization. But the amount was so small that a very small error in the determination of either the arsenic or sulfur renders the results useless; thus, in one case an error of 0.1% in analysis made an error of 100% in the calculation of hydrogen sulfide of peptization.

Since a quantitative study of this mutual reaction is precluded, at least a qualitative test is justifiable. If in the mutual precipitation of ferric oxide sol and arsenious sulfide sol a chemical reaction takes place between the ferric chloride and hydrogen sulfide of peptization, one of the following reactions may take place: (1) $H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + S + 2HCl$; (2) $3H_2S + 2FeCl_3 \longrightarrow 2FeS + S + 4HCl$.

In most precipitations there is no evidence of the latter reaction, as the precipitate is yellow. When, however, the sol contains a great amount of hydrogen sulfide, a blackening develops which can be explained by the formation of ferrous sulfide.

⁵ Ward, Am. Chemist, 4, 10 (1873).

To test the supposition that the mutual precipitation between ferric oxide sol and arsenious sulfide is due to the oxidation of the sulfide ion of the peptizing hydrogen sulfide by the ferric ion of the peptizing ferric chloride, the following experiment was performed.

Five hundred cc. of an arsenic trisulfide sol was precipitated with ferric oxide sol No. 4, the precipitate dried and extracted with carbon disulfide. Sulfur was recovered. Since arsenious sulfide sols are most likely to contain sulfur after exposure to air, a "blank" was run wherein an equal quantity of sol was precipitated by aluminum sulfate, the precipitate dried, extracted, and the sulfur found subtracted from that obtained in the main experiment.

It has been generally considered that hydrogen sulfide is always the stabilizing agent of arsenic trisulfide sols. In this investigation it was found that sols that contained an excess of arsenious acid, either through decomposing the arsenic trisulfide and driving out some hydrogen sulfide, or by failure to add an equivalent or slight excess of the hydrogen sulfide for the arsenious acid in solution when preparing the sols, were very stable. They gave a sharp range of precipitation with the ferric oxide sols, if sufficiently dilute, and acted in every way as did the arsenic trisulfide sols peptized by hydrogen sulfide. They have the advantage of having a nonvolatile peptizing agent, and one that does not oxidize as readily as does hydrogen sulfide, thus being more dependable for quantitative work. The arsenic trisulfide sols peptized by arsenious acid will probably be found more satisfactory for further quantitative work on the mutual precipitation of ferric oxide and arsenic trisulfide sols than those peptized by hydrogen sulfide have been.

Summary

- 1. The precipitating ratios of certain mutually precipitating hydrosols depend upon the peptizing agent.
- 2. There is chemical equivalence between the peptizing agents of ferric oxide hydrosol peptized by ferric chloride, and silicic acid sols peptized by sodium silicate, provided the ratio of peptizing agent to the dispersed phase falls within a certain range. Outside of this range the precipitation is erratic.
- 3. Ferric-oxide—silicic-acid sol precipitations showing chemical equivalence between the peptizing agents at maximum precipitation exhibit little variance in precipitation ratios with dilution, while those showing a divergence from chemical equivalence approach chemical equivalence with dilution.
- 4. Mutual precipitation of ferric oxide and silicic acid sols is due to the removal of peptizing agents by chemical reactions between them.
- 5. Qualitative experiment shows that the mutual precipitation of arsenious sulfide hydrosol and ferric oxide hydrosol may be due to the

chemical reaction $S^{--} + 2Fe^{+++} \longrightarrow S^{\circ} + 2Fe^{++}$. It was impossible to verify this quantitatively because of restrictions in the analytical procedures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL, UNIVERSITY]

AZIDO-CARBONDISULFIDE. I. FORMATION, PREPARATION AND GENERAL PROPERTIES¹

By A. W. Browne, A. B. Hoel, G. B. L. Smith and F. H. Swezey With Microscopical Studies by C. W. Mason Received July 21, 1923

It was found by F. Sommer,² during an investigation of the properties of sodium azido-dithiocarbonate, that treatment of aqueous solutions of this salt with such oxidizing agents as ferric chloride, iodine in potassium iodide, and potassium permanganate, potassium dichromate, or ceric salts in sulfuric acid solution, results in the precipitation of an unstable white solid, surmised by him, from the method of its formation, to possess the formula N₂—N—CS—S—CS—N—N₂. No analysis was made of this compound, or study of its properties, aside from the observation that a sample of the insoluble needles, when heated under water, exploded violently at a temperature below 100°.

The formation of this substance, to which the name azido-carbondi-sulfide is provisionally assigned, has been repeatedly observed in this Laboratory³ to take place when aqueous solutions of potassium trinitride and iodine are brought together under certain conditions in the presence of carbon disulfide. Azido-carbondisulfide has been shown to have an important catalytic effect upon the reaction between potassium trinitride and iodine, as does the related compound, potassium azido-dithiocarbonate. In fact, these two substances, the relationship between which is very similar to that between iodine and potassium iodide, behave in this reaction in the manner characteristic of what might be termed a reciprocal catalytic pair.⁴

Formation and Preparation.—The action of various oxidizing agents

- ¹ The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article No. 4 under Heckscher Grant No. 4. For Articles 1, 2, and 3 see This Journal, 44, 2106, 2116, 2315 (1922). This paper was presented at the New Haven meeting of the American Chemical Society in April, 1923.
 - ² Sommer, Ber., 48, 1833 (1915).
 - ³ Browne and Hoel, This Journal, 44, 2106 (1922).
- ⁴ This term is intended to apply to any pair of chemical compounds that undergo repeated mutual conversion into each other while having their catalytic effect upon a given chemical reaction.

upon a 3% aqueous solution of potassium azido-dithiocarbonate has been investigated. Unless otherwise specified, a 1% solution of the oxidizing agent was gradually added in each case to 5 cc. of the azido-salt solution in a test-tube.

Hydrogen peroxide causes evolution of gas and produces a transitory, vellow-green color. The solution soon becomes turbid, and a considerable amount of azido-carbondisulfide is ultimately precipitated. Ozonized oxygen, when bubbled through the azido-salt solution, causes a slight evolution of gas. Potassium iodate and potassium chromate yield a small amount of precipitate after standing for several hours. With potassium persulfate, characteristic crystals of the azido-disulfide appear after a time. Mercuric chloride precipitates at once a heavy, white, crystalline substance, probably mercuric azido-dithiocarbonate, and later yields a fluffy, white precipitate of the azido-disulfide. In the presence of a slight excess of hydrochloric acid, ferric chloride first turns the solution red, and ultimately precipitates the azido-disulfide. Under similar conditions stannic chloride shows no action at first, but later forms a white precipitate. In the presence of sulfuric acid, potassium permanganate, solid manganese dioxide, solid cerium dioxide and sodium nitrite produce sooner or later the insoluble azido-disulfide, accompanied in the last case by evolution of considerable gas and appearance of a temporary brown color in the solution. Chlorine, bromine and iodine yield at once an abundant precipitate of the azidodisulfide.

Electrolysis of an approximately 20% solution of potassium azidodithiocarbonate between a rotating platinum anode of 30 sq. cm. total area and a stationary platinum cathode enclosed in a parchment thimble, with anode current density of 18.6 amp./sq. dm., resulted in the formation of relatively large amounts of azido-carbondisulfide, small particles of which occasionally exploded, under the solution, at or near the anode, with a sharp, crackling noise.

The method finally selected for the preparation of azido-carbondisulfide involves the following procedure.

Five cc. of the clear, concentrated solution of potassium azido-dithiocarbonate, obtained by filtering the liquid resulting from interaction of 6 g. of potassium trinitride and 6 g. of carbon disulfide in 25 cc. of water, is diluted with 50 cc. of water. Normal iodine solution in potassium iodide is added drop by drop, with continual stirring, until complete precipitation of the azido-disulfide has been effected. The slightest excess of free iodine must be avoided, however, as iodine appears to be adsorbed by the disulfide, and can be removed from it by washing only with some difficulty. If an excess of iodine be inadvertently added this may be reduced by addition of the requisite amount of a dilute solution of the azido-salt. The possible formation of an intermediate product such as iodine azido-dithiocarbonate, ISCSN₃, will be considered in a later investigation.

The precipitated azido-disulfide is washed in a Büchner funnel with cold water until free from soluble material, and is partially dried by suction. Small portions are carefully spread upon a porous plate with the aid of a bone spatula, avoiding tapping or undue

pressure, and are finally stored in a desiccator over phosphorus pentoxide, kept at 10° or lower, to minimize spontaneous decomposition.

Analysis.—Sulfur was determined in the thoroughly dried crystals of azidocarbondisulfide by oxidizing weighed samples with coned. nitric acid and bromine, and weighing the sulfur in the form of barium sulfate.

Analyses. Subs., 0.2251, 0.2002: BaSO₄, 0.8911, 0.7943. Calc. for $(SCSN_3)_2$: S, 54.27. Found: 54.37, 54.49.

Nitrogen was determined by combustion of the azido-disulfide in the manner already employed for potassium azido-dithiocarbonate.⁵

Analyses. Subs., 0.0567, 0.1890: N_2 , 16.12 cc. (0.02016 g.), 53.83 cc. (0.06733 g.). Calc. for $(SCSN_3)_2$: N, 35.57. Found: 35.56, 35.62.

These results point toward the formula suggested by Sommer for this compound and, in connection with the data concerning its decomposition submitted below, tend to confirm the following structure.

Properties.—Azido-carbondisulfide is a white, crystalline solid, soluble to the extent of about 3 parts in 10,000 of water at 25°. It is very unstable, and is distinctly more sensitive to impact and to heat than is potassium azido-dithiocarbonate. Explosions have frequently occurred at various stages of its preparation and investigation. These explosions result in the liberation of much heat, with more smoke but less flame than is characteristic of explosions of the azido-dithiocarbonate.

Three consecutive attempts to effect the slow, quantitative decomposition of weighed samples of the dry azido-disulfide, varying from about 0.06 to 0.17 g. in weight, by careful heating in a glass tube connected with a nitrometer, and immersed in a waterbath, resulted in violent explosions, in the first case at 54°, and in the second and third at 50°. Qualitative proof of the evolution of nitrogen and of the presence of thiocyanates in the residue and in the water above the mercury in the nitrometer tube was nevertheless obtained in the second experiment.

In a fourth experiment, 0.1097 g. of azido-carbondisulfide was held at 40° for 3 hours, with the result that 20.54 cc. (corr.) or 0.02569 g. of nitrogen, corresponding to 3.95 atoms of nitrogen per molecule of the disulfide, was liberated. Continued heating for a number of hours to an ultimate temperature of 60° increased the volume to 20.83 cc. (corr.) corresponding to 0.02605 g. of nitrogen, or 4.005 atoms of nitrogen per molecule of the compound.

Azido-carbondisulfide undergoes gradual spontaneous decomposition at ordinary room temperatures, with liberation of nitrogen, and formation of a solid residue probably consisting of a mixture of free sulfur and polymeric thiocyanogen,⁶ in accordance with the equation

$$(SCSN_3)_2 = 2N_2 + 2S + (SCN)_2$$
 (1)

A freshly prepared sample of the azido-disulfide weighing 0.1145 g. was placed in the nitrometer tube, which was immersed in a thermostatic

⁵ Browne and Hoel, This Journal, 44, 2315 (1922).

⁶ Söderbäck, Ann., 419, 217 (1919).

bath and held at 25° under close observation for a period of 72 consecutive The volume of nitrogen evolved was read at intervals of 1 or 2 hours. The data obtained are shown in Figs. 1 and 2.

These curves show clearly that the velocity of the decomposition, which has hitherto undergone a remarkably regular acceleration, begins to decrease as soon as two atoms, or 1/2 of the available nitrogen, has been evolved. This may indicate that the decomposition of azido-carbondisulfide takes place in two stages, with initial formation of an inter-halogenoid substance, azido-carbondisulfide thiocyanate, intermediate in

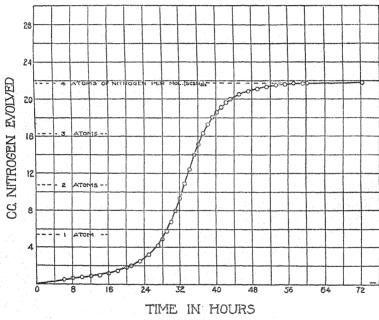


Fig. 1

composition between azido-carbondisulfide itself, and dithiocyanogen, in accordance with the equation

$$(SCSN3)2 = N2 + S + SCSN3.SCN$$
 (2)

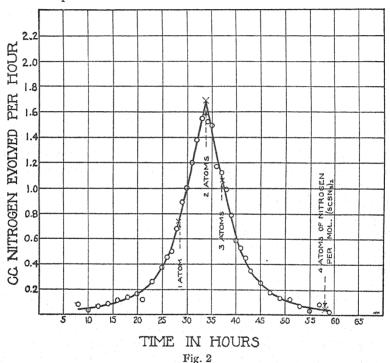
This intermediate product may then decompose more slowly, during the second stage of the reaction, as expressed by the equation

$$SCSN_3.SCN = N_2 + S + (SCN)_2$$
 (3)

During the decomposition of azido-carbondisulfide a very noteworthy change of color gradually takes place. In one experiment, typical of the many that have been performed, a sample of the pure white compound, after standing at room temperature (about 25°) for 23 hours, assumed a very light yellow color, YT2 on the Milton Bradley Standard.7 After

⁷ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons. New York, 1st ed., 1905, vol. I, p. 232.

successive time intervals further changes in color resulted as follows: 4 hours, YT1; 16, OY; $3^1/2$, YO; $3^1/2$, O; 2, RO; $15^1/2$, RO-OS1; 7, OS1. The dark orange color thus attained, after a total period of nearly 75 hours, remains unchanged for an indefinite length of time. This series of changes seems to be in no way dependent upon the degree of illumination to which the material is subjected. One sample, exposed for some time to direct (July) sunlight, showed changes in color identical with those of a sample kept in a dark cupboard. The rate of change, however, varies directly with the temperature.



Under the microscope, crystals of the freshly prepared azido-carbondisulfide are seen to be colorless, and of tabular prismatic to acicular habit. For this reason end views are not obtainable. All prismatic views exhibit parallel extinction and fairly strong double refraction. The lower index of refraction corresponds to vibrations parallel to the elongation of the crystals. The mean index of refraction cannot readily be determined, on account of the solubility of the crystals in the various immersion liquids (essential oils), but it is estimated at about 1.8. The crystals show faces corresponding to the prism, bipyramid of a different order, and rarely the basal pinacoid. Tabular crystals, 6-sided in outline, exhibit terminal angles of about 138°. Asymmetric forms are frequent, particularly those in which 2 or 4 of the pyramid faces are not developed, giving rise to 5-sided or to trapezoidal outlines. At the ends of the crystals V-shaped markings are frequent. The habit and all observable optical properties lead to the classification of the crystals in the tetragonal or in the orthorhombic system.

When newly precipitated, dry azido-carbondisulfide is allowed to decompose at room temperature on a microscope slide, the crystals show surface corrosion after about 24 hours, and are coated with a yellow, viscous substance. Gas evolution takes place coincidently with a progressive corrosion or decomposition of the crystals from the surface inward, and not infrequently an isolated crystal is seen at this stage to be almost completely decomposed, a fragment remaining for a time imprisoned in the center of the viscous, amber liquid. Starting again at the outside, the decomposition product gradually becomes more viscous and also grows darker in color, yielding, in about 48 hours, after further evolution of gas, a reddish-orange, brittle, amorphous, vesicular mass, particles of which may retain something of the form of the original crystals. The final product, as seen by transmitted light, is of a somewhat greenish-yellow appearance in thin layers, while in thicker layers it is of a reddish-orange tint.

When a dried sample of the azido-disulfide is heated on a microscope slide it explodes, leaving an oily, viscous, yellow residue, apparently identical with the product of partial decomposition at room temperature. In case the detonation has been effected in such a way as to avoid heating of the slide, as by touching the sample for an instant with a hot platinum rod or wire, or by quickly passing a flame over it, the resulting liquid is of a very pale yellow color, and remains for some time entirely free from gas bubbles. If, on the other hand, the slide is heated, transformation of the yellow product into the usual brittle, vesicular mass, which would be formed in any event after the lapse of some time, soon takes place with comparatively rapid evolution of gas.

The yellow oil obtained as an intermediate product during the decomposition of azido-carbondisulfide is probably not identical with the amorphous thiocyanogen obtained, also in the form of a "clear, thick, yellow oil," by Söderbäck,8 but may consist of a solution of still unchanged azido-carbondisulfide in thiocyanogen, or of an inter-halogenoid compound, SCSN₃. SCN, as suggested in an earlier paragraph, mixed with free sulfur. Except for the presence of this free sulfur, the dark orange (OS1), brittle, vesicular product finally obtained, after further spontaneous liberation of gas from the yellow oil, is probably identical, however, with Söderbäck's "brick-red, light substance" obtained when the yellow oil was gently heated in a vacuum, or with his spontaneously formed "yellow-brown or yellow-red resin."

The yellow oil obtained as an intermediate product, either by spontaneous decomposition at room temperature or by careful detonation of azido-carbondisulfide, has been found to have a marked catalytic effect upon the decomposition of the disulfide. Freshly prepared samples of the oil, when brought into contact with undecomposed portions of azido-

⁸ Ref. 6, p. 237.

carbondisulfide, start at once a decomposition at a rate apparently equal to the maximum velocity of spontaneous decomposition at the temperature chosen. After the oil has itself undergone the second stage of decomposition, with formation of the resinous product, it loses its catalytic power.

As a result of the vesicular and resinous character of the decomposition product considerable difficulty was experienced in effecting a quantitative separation of the free sulfur from the polymeric thiocyanogen. Three methods were investigated: (1) prolonged heating of the mixture to 125°, until no further vaporization of sulfur takes place; (2) extraction with carbon tetrachloride; and (3) extraction with carbon disulfide. The last method yielded the best results. A sample of the dark orange mixture, weighing 3.6486 g., was extracted with carbon disulfide in a Soxhlet apparatus for a period of 100 hours, after which further treatment effected the separation of no additional sulfur.

The percentage of sulfur contained in the residue was determined, with the following results.

Subs., 0.4980, 0.4997: BaSO₄, 2.0065, 2.0188. Calc. for (SCN)_x: S, 55.21. Found: 55.33, 55.48.

These data indicate that the residue was a fairly pure, polymerized thiocyanogen. Further work upon this product will be carried on, in order to determine its molecular weight, and to investigate its properties and reactions.

Behavior toward Non-Aqueous Liquids.—Azido-carbondisulfide is appreciably soluble in methyl alcohol, ethyl alcohol, diethyl ether, carbon tetrachloride and xylene. It is moderately soluble in benzene and in carbon disulfide, and more readily soluble in ethyl acetate and in acetone. A sample weighing 0.1180 g., for example, was easily taken up by 1.4 cc. of acetone.

Solutions of azido-carbondisulfide in these liquids undergo gradual spontaneous decomposition at room temperature, with deposition of solids ranging in color from yellow to dark orange (OS1) and resembling in composition the residue obtained by decomposition of the solid solute. In some instances a secondary product is formed, probably as a result of the action of the freshly liberated thiocyanogen, SCN or (SCN)₂, upon the solvent. The velocity of decomposition is very much greater in some cases than that of the dry solute.

Xylene solutions show a slow evolution of gas almost at once, assume a yellow color, and soon begin to deposit droplets of a yellow, viscous substance. The final product possesses an odor closely resembling that of scorched rubber. Acetone solutions yield a dark orange (OS1) residue possessing a strong odor of garlic.

Behavior toward Acids.—Dil. sulfuric acid (1:6) shows little or no action upon azido-carbondisulfide at room temperature. At 40° the solid

slowly dissolves, and the resulting solution gradually becomes turbid owing to the liberation of sulfur. More concentrated acid (1:1) attacks the solid slowly even at room temperature, while the undiluted acid effects a more rapid reaction, accompanied by an appreciable evolution of gas.

Hydrochloric acid reacts with azido-carbondisulfide somewhat more readily than does sulfuric acid, with liberation of sulfur and evolution of gas. The residual solution obtained when concd. acid was used as the solvent was found to contain thiocyanates as well as an oxidizing agent capable of liberating iodine from a solution of sodium iodide. This action is attributable either to free chlorine, to thiocyanogen, or to an interhalogen-halogenoid compound such as chlorine azido-dithiocarbonate, CISCSN₃, or chlorine thiocyanate, CISCN.

Nitric acid in corresponding concentrations behaves in much the same way as hydrochloric acid, except that no precipitation of sulfur takes place. Acetic acid reacts somewhat less vigorously than the mineral acids, although the concd. acid promptly dissolves the solid azido-disulfide at room temperature, yielding a solution that is clear at first, but that becomes turbid after a time.

Behavior toward Alkalies.—Azido-carbondisulfide reacts at once with solutions of potassium hydroxide, yielding a clear, greenish-yellow solution. At room temperatures the liberation of small amounts of gas takes place immediately, and is followed by a very slow, long-continued evolution of gas as the unstable product is gradually decomposed. At low temperatures no perceptible evolution of gas occurs. For example, when about 3 cc. of a 10 N solution of potassium hydroxide was treated at —10° with the solid halogenoid, the usual greenish-yellow solution was formed, without liberation of gas. The reaction, in its initial stage, probably takes place in accordance with the equation

$$(SCSN_3)_2 + 2 KOH = KSCSN_3 + KOSCSN_3$$
 (4)

with formation of potassium azido-dithiocarbonate and potassium azido-oxydithiocarbonate, respectively, analogous to the chloride and hypochlorite formed by interaction of free chlorine and potassium hydroxide. Acidification of the greenish-yellow solution with dil. sulfuric acid in slight excess causes the precipitation of azido-carbondisulfide, as follows.

$$KSCSN_3 + KOSCSN_3 + H_2SO_4 = K_2SO_4 + (SCSN_3)_2 + H_2O$$
 (5)

This corresponds to the liberation of chlorine by acidification of a solution containing a chloride and a hypochlorite. The filtrate obtained on removal of the solid halogenoid was found to contain relatively large amounts of the azido-salt. This was shown by the abundant precipitation of azido-carbondisulfide that took place on addition of a solution of iodine, and by the vigorous catalytic action exerted by even a minute amount of the filtrate upon the reaction between iodine and potassium

trinitride. These point toward the conclusion that at least a part of the azido-dithiocarbonate, or hypochlorite analog, has undergone transformation to a derivative containing a larger amount of oxygen, such as the azido-trioxydithiocarbonate, or chlorate analog, as expressed by the equation

$$3 \text{ KOSCSN}_3 = 2 \text{ KSCSN}_3 + \text{ KO}_3 \text{SCSN}_3$$
 (6)

This chlorate analog may be regarded as a derivative of sulfuric acid obtained by replacement of an hydroxyl by the azido-thiocarbonyl group, CSN₂. On this assumption, the compound might easily hydrolyze in aqueous solution, especially after acidification with hydrochloric acid, yielding free sulfuric acid as one product. The presence of sulfuric acid in considerable amount has been established experimentally by repeated examination of the solutions obtained by interaction of azido-carbondisulfide and potassium hydroxide. 10 It is of course possible that the appearance of sulfuric acid may be due partly or wholly to the formation of potassium oxythiocyanate, KOSCN, by decomposition of the azidooxydithiocarbonate, and subsequent transformation of this hypochlorite analog of the thiocyanogen series to the chlorate analog, KO₃SCN, which in acid solution should hydrolyze, yielding sulfuric and hydrocyanic acids. Söderbäck,11 while apparently overlooking the analogy between cyanosulfuric and chloric acids, has demonstrated the formation of sulfuric and hydrocyanic acids as products of the hydrolysis of free thiocyanogen. The absence of hydrocyanic acid from the products of hydrolysis of azido-carbond sulfide, however, points toward the conclusion that the sulfuric acid is not in this case formed by way of the thiocyanogen derivatives, but that the new halogenoid probably forms its own series of oxyacids.

With solutions of sodium hydroxide, ammonium hydroxide, and sodium carbonate, azido-carbondisulfide was found to react as with a solution of potassium hydroxide, yielding the characteristic greenish-yellow solution.

Behavior toward Certain Oxidizing Agents and Reducing Agents.—Azido-carbondisulfide readily reduces potassium permanganate at room temperature in neutral, alkaline or acid solution. It reacts with potassium iodate in neutral and in acid, but apparently not in alkaline solution. A 3% solution of hydrogen peroxide slowly dissolves the disulfide, yield-

⁹ It has been found that potassium thiocyanate also has a marked catalytic effect upon the reaction between iodine and potassium trinitride, and it is thought that potassium thiocyanate and free thiocyanogen may, like potassium azido-dithiocarbonate and azido-carbondisulfide, constitute a reciprocal catalytic pair.

¹⁰ The experimental work on this topic has been performed in this Laboratory by Mr. Frank Wilcoxon, who first called attention to the presence of sulfuric acid among the products of this reaction.

¹¹ Ref. 6, p. 294.

ing a solution which has the odor of hydrocyanic acid.¹² The reaction seems to take place less rapidly in the presence of dil. sulfuric acid. The greenish-yellow color of the dilute alkaline solution containing sodium hydroxide is discharged by hydrogen peroxide, with evolution of gas.

Successive portions of azido-carbondisulfide added to a fairly concentrated aqueous solution of hydriodic acid cause immediate liberation of iodine, the color of which soon disappears, owing to a secondary reaction that possibly results in the formation of iodine azido-dithiocarbonate or iodine thiocyanate. Dilute aqueous hydrazine hydrate dissolves the disulfide at once, with slow evolution of gas, yielding a solution which is at first colorless, but later assumes a light greenish-yellow color (GYT2), and deposits a light gelatinous precipitate. Five per cent. solutions of ferrous sulfate, stannous chloride, and oxalic acid show no appreciable immediate reducing action upon azido-carbondisulfide.

Further work upon many of the topics briefly mentioned in the present article is now in progress in this Laboratory, and will be made the subject of future communications.

Summary

Azido-carbondisulfide, (SCSN₃)₂, a new halogenoid substance, has been prepared by chemical or electrochemical oxidation of potassium azido-dithiocarbonate, KSCSN₃, and its composition has been established by analysis. It is a white, crystalline solid, very slightly soluble in water, but readily soluble in certain non-aqueous liquids, such as acetone and ethyl acetate. It is stable at 0°, but undergoes quantitative autocatalytic decomposition at room temperature, yielding polymeric thiocyanogen, sulfur and nitrogen gas.

A preliminary study has been made of the behavior of azido-carbondisulfide toward acids and alkalies, and toward certain oxidizing agents and reducing agents.

ITHACA, NEW YORK

 $^{^{12}}$ Kastle and Smith $[Am.\ Chem.\ J.,\ 32,\ 376\ (1904)]$ have shown that thiocyanic acid is oxidized by hydrogen peroxide, with formation of sulfuric acid and hydrocyanic acid, probably in accordance with the equation, HSCN $+\ 3H_2O_2=HCN+H_2SO_4+2$ H_2O . The possible formation of cyano-sulfuric acid, the analog of chloric acid, as an intermediate product of this reaction, should be borne in mind. See also Bjerrum and Kirschner, Kgl. Danske Vidensk. Selskab. Math. Medd., [8] V, No. 1, 76 pp. (1918); C. A., 13, 1057 (1919).

[Contribution from the Chemical Laboratory of Clark University, No. 1, 30]

THE RESISTANCE-TEMPERATURE COEFFICIENT OF CONCENTRATED SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA AND THE SPECIFIC CONDUCTANCE OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA AT INTERMEDIATE CONCENTRATIONS

By Charles A. Kraus and Walter W. Lucasse

RECEIVED JULY 23, 1923

In a preceding article¹ the authors have given the results of an investigation on the resistance-temperature coefficient of concentrated solutions of sodium in liquid ammonia. It appeared of interest to carry out a similar series of measurements with solutions of potassium in liquid ammonia at concentrations up to the saturation point. In the case of solutions of sodium in liquid ammonia, it was not possible to measure the temperature coefficient at lower temperatures over a considerable concentration interval, owing to the fact that this system separates into two phases with a critical point at -41.6° .²

The method and apparatus employed were the same as those previously employed in the case of sodium solutions. The results obtained, however, are on the whole more consistent than those obtained with sodium, partly because of the larger temperature interval which could be here employed and partly because of greater experience in the manipulation of the apparatus.

The Resistance-Temperature Coefficient of Potassium in Liquid Ammonia as a Function of Concentration.—Three independent series of measurements were carried out with solutions of potassium in liquid ammonia. Excepting the first two points in Series 1, the temperature interval employed was from the boiling point of liquid ammonia to -45° . The results are given in Table I, in which the dilution V, in liters of pure ammonia per gram-atom of potassium, is given in the first column; the upper temperature, in the second column; the lower temperature, in the third column; and, in the fourth column, the resistance-temperature coefficient:

$$\gamma = \frac{1}{R_{-33.5}} \frac{\Delta R}{\Delta t} \times 100.$$

The results are shown graphically in Fig. 1 in which the temperature coefficients are plotted as ordinates and the dilutions V, as defined above, as abscissas. The curve is similar to that obtained in the case of solutions of sodium in liquid ammonia, but is not identical with it. At the lower concentrations, the potassium solutions yielded a minimum coefficient of 1.42% as against 1.52% for sodium. At the higher

¹ Kraus and Lucasse, This Journal, 44, 1941 (1922).

² Kraus and Lucasse, ibid., 44, 1949 (1922).

4.50

4.50

4.55

3.04

2.22

1.85

32.9

32.9

0.88

33.0

33.0

33.0

0.8933

0.9462

1.9120

1.409

1.879

2.443

45.0

45.0

45.0

45.0

45.0

45.0

3.882

4.508

5.285

6.081

5.140

4.018

33.05

33.05

33.1

33.1

33.1

33.1

45.0

45.0

45.0

45.0

45.0

45.0

1.56

1.47

1.48

1.42

1.46

1.49

concentrations, the temperature coefficient in the case of potassium is markedly higher than in that of sodium. The maximum value is 4.55%

			TABL	EΙ				
RESIS:	rance-Te	MPERATURE	COEFFICIENT	OF	Potassium	IN LI	ршь Ам	MONIA
V	t_1	12	γ		V	t_1	12	γ
	Series	: 1				Seri	ies 2	
0.1250	-32.9	-40.0	0.0438		0.4018	-32.8	-45.0	0.806
.1297	33.1	40.1	0.0880		0.5200	32.8	45.1	1.57
.1538	33.0	45.1	0.132		0.5611	32.8	45.0	1.90
,2046	33.0	45.1	0.208		0.6501	32.8	45.0	2.80
.2831	33.0	45.0	0.388		0.7145	0.88	45.0	3.43
.3565	33.0	45.0	0.613		0.8054	0.88	45.0	4.22
.4385	0.88	45.0	1.02		0.9863	33.0	45.0	4.41
	Se	ries 3			1.167	33.0	45.0	3.91
3.141	-33.05	-45.0	1.67		1.079	32.9	45.0	4.16

per degree, whereas that of sodium is approximately 3.6%. This difference may in part be due to the fact that the temperature interval in the case of the potassium solutions is markedly greater than in that of the

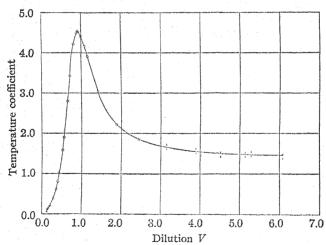


Fig. 1.—Variation of temperature coefficient of solutions of potassium in liquid ammonia as a function of concentration

sodium solutions; while at the same time the temperature coefficient increases with decreasing temperature. The maximum value of the temperature coefficient occurs at a dilution of approximately 1.15 liters in the case of sodium, while in that of potassium solutions it lies at a dilution of 0.91 liters.

Beyond the maximum, the temperature coefficient falls off very rapidly to a value of 0.0438% per degree for the saturated solution, which does not differ greatly from the corresponding coefficient of a solution of sodium. In the case of potassium, as in that of sodium, the coefficient would have a negative value if the concentration of the metal were slightly higher.

The Resistance-Temperature Coefficient as a Function of Temperature.—The resistance-temperature coefficient of solutions of potassium in liquid ammonia was measured at a series of temperatures down to approximately -70° for concentrations up to approximately normal. The results are given in Table II, in which the point in the series is given in the first column, the dilution V in the second column, the limits of the temperature intervals in the third and fourth columns, and the value of the coefficient γ in the last column.

Table II

Resistance-Temperature Coefficients of Potassium Solutions in Liquid Ammonia for Different Temperature Intervals

Point No.	· · · · · · · · · · · · · · · · · · ·	<i>t</i> ₂	<i>t</i> 2	γ
1	0.1250	-32.9	-40.0	0.0438
		40.0	50.0	0.0918
		50.0	60.0	0.119
		60.0	67.0	0.122
2	0.1303	33.1	25.5	0.0537
	0.1297	33.1	40.1	0.0880
		40.1	50.1	0.103
		50.1	60.1	0.119
		60.1	67.5	0.155
12	0.9099	33.0	40.0	4.35
		40.0	50.0	5.30
		50.0	60.0	6.73
		60.0	70.2	7.29
	0.9120	33.0	45.0	4.55

The results here obtained are again similar to those obtained in the case of solutions of sodium. With decreasing temperature, the value of the coefficient increases. This is particularly marked at the higher concentrations, where the temperature coefficient increases approximately three times in passing from the interval of -32.9° to -40° to that of -60° to -67° . Very remarkable is the value which the coefficient assumes for the interval -60° to -70° , at a concentration in the neighborhood of the maximum, which amounts here to 7.29%.

Up to the present time it is not possible to indicate the factors to which the variation of the temperature coefficient may be due. It is a fact, however, that, at higher concentrations, the density of solutions of the alkali metals in liquid ammonia undergoes a phenomenally large change, the density increasing with decreasing concentration.³

The Specific Conductance of Solutions of Potassium in Liquid Ammonia at its Boiling Point at Intermediate Concentrations.—In an earlier paper the authors have given data on the specific conductance of solutions of potassium in liquid ammonia by direct comparison with mercury at dilutions as high as V=0.7229. Since that time a further series of measurements has been made carrying the dilution to V=1.597. The results are given in Table III, in which the dilution, as defined above, appears in the first row, and the specific conductance l in reciprocal ohms, in the second.

TABLE III

Specific Conductances of Solutions of Potassium in Liquid Ammonia at -33.5° V.... 0.3205 0.4031 0.4881 0.5782 0.7310 0.8893 1.240 1.597 1... 692.8 359.2 174.4 78.65 19.95 6.279 1.415 0.7470

The results of this series of experiments are in accord with those previously recorded and require no further comment. Attention should be called to a typographical error in an earlier paper, where the value of the equivalent conductance as given under Observation No. 1, in Table III, at dilution V=0.4229 should read "125,600.0." Calculating the value of the specific conductance of a lithium solution from this value, it is found to correspond very closely with the value for solutions of sodium and potassium at the same concentration.

Summary

The resistance-temperature coefficient of concentrated solutions of potassium in liquid ammonia has been measured from a dilution of 6 liters to the saturation point. The change of the temperature coefficient as a function of the concentration parallels that previously observed in the case of solutions of sodium. At higher concentrations, the temperature coefficient is somewhat greater for solutions of potassium than for sodium and the maximum temperature coefficient is found at a somewhat higher concentration.

The temperature coefficient has been measured as a function of the temperature at a number of concentrations. The temperature coefficient increases as the temperature decreases and the percentage change of the coefficient is greater at higher concentrations.

Some additional values are given for the specific conductance of potassium solutions in liquid ammonia at certain intermediate concentrations. These agree with previous observations.

³ Unpublished observations in this Laboratory.

⁴ Kraus and Lucasse, This Journal, 43, 2529 (1921).

⁵ Kraus, *ibid.*, **43**, 756 (1921).

This investigation has received support from the Warren Fund of the American Academy of Arts and Sciences, of which aid we wish to express our grateful acknowledgment.

Worcester, Massachusetts

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A STUDY OF THE TERNARY SYSTEM, TOLUENE-ACETONE-WATER

By James H. Walton and John D. Jenkins RECEIVED JULY 23, 1923

Toluene and acetone are miscible in all proportions, as are also acetone and water. Water and toluene, however, are practically insoluble in each This investigation was undertaken for the purpose of determining the solubility curve for these three compounds.

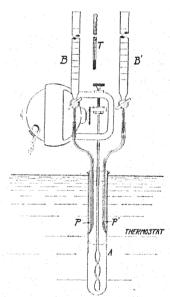
Reagents.-Acetone was dried over calcium chloride and fractionated, the fraction distilling between 56.05° and 56.16° at 760 mm. being used.

The toluene was dried over sodium, distilled and fractionated. The fraction boiling between 110.65° and 110.75° at 760 mm. was collected.

The water used was a high grade of conductivity water.

Apparatus and Method.—The pipets, burets and flasks were carefully calibrated with air-free water and the pipet also with toluene.

The apparatus in which the determinations were made is shown in Fig. 1. A is a 20 × 2.5cm. testtube in which the liquids were mixed; P and P' are two capillary delivery tubes, leading from the burets B and B' containing the acetone and one of the other liquids. The method of making a determination was A definite amount, usually 10 cc., of either water or toluene was pipetted into the testtube, which was then immediately stoppered, placed in the thermostat and allowed to stand for 15 minutes to come to the temperature of the bath. A small amount of the immiscible liquid, 0.2 to 0.5 cc., was then slowly added, the mixture vigorously stirred by means of the motor stirrer and acetone run in slowly, until the solution just cleared. The volumes of the Fig. 1.-Apparatus used for solliquids were then read and the temperatures of the burets noted. A new portion of the immiscible liquid



ubility determinations

was then added, and the process repeated. This was continued until the test-tube was about $^{2}/_{3}$ full, when another run was made in exactly the same manner, starting with the other immiscible liquid in the test-tube. This was found necessary because of the small solubility of one liquid in the other in the presence of a small percentage of acctone.

In order to obtain satisfactory determinations of the parts of the curves where there is only a small percentage of one component in the other (toluene in water, for example), it was found necessary to make a solution of this component in acetone, so that the volumes could be more accurately measured. For this purpose, a 20% solution in acetone was found convenient. The solution was made by weighing 20 cc. of the toluene into a 100cc. flask, filling to the mark with acetone and weighing again.

Because of the high coefficient of expansion of acetone, about 1.00145 per degree at 30°, great care was necessary to control the temperature of the solution. The flask was allowed to come to constant temperature in a thermostat for 15 minutes before it was finally made up to the mark. This solution, which was used in the buret instead of pure liquid, permitted accurate determinations down to about 0.05 cc. of one component in 10 cc. of the other.

The temperature of the liquids in the burets was taken as the average of several readings of the thermometer "T" during the run, the fluctuations usually not being more than a fraction of a degree. The temperature of the liquid placed in the tube was noted at the time it was added from the pipet and its weight and the weights of the others were calculated from their densities at their respective temperatures.

The end-point was taken as the point at which a bright object placed behind the test-tube became sharply defined. It was very sharp between the range of from 5% to 40% of water and especially between 5% and 15% of water. Between the range 15% to 30% of water, the mixture had a very decided colloidal appearance at the end-point, this effect being at a maximum with 20% water. The end-point was very distinct through this whole range, half a drop of acetone being sufficient to change the mixture from a distinct silky appearance, when rapidly stirred, to a distinctly cloudy, but transparent solution. Before adding the half drop, the mixture slowly separated into two layers, but afterward no separation occurred even on prolonged standing. On further additions of successive portions of acetone, the milkiness gradually disappeared, 0.5 to 1 cc. being required to make it disappear entirely.

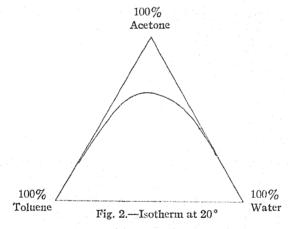
Data

Determinations were made at three temperatures: 0° , 20° and 30° . Four runs were made for each curve, first starting with 20 cc. of toluene in the tube and adding a 20% solution of water in acetone, and acetone, from the burets; second, with 10 cc. of toluene, adding water and acetone; third, with 10 cc. of water, adding acetone and toluene; and fourth, with 20 cc. of water, adding acetone and a 20% solution of toluene in acetone. These runs overlapped to some extent, the first extending from 0.5% water to 5% water, the second from 1.3% water to about 19%, the third from 17% water to 50% and the fourth from 47% water to about 80%. The parts of the curves overlapping checked very closely in all cases.

Table I Data for Equilibrium Line between the One-Liquid Phase and Two-Liquid Phase and Two-Liquid Phase Systems at 0°

		All percentages a	re by weight		
% Water	% Toluene	% Acetone	% Water	% Toluene	% Acetone
0.5	70.3	29.2	15.0	17.5	67.5
1.0	60.0	39.0	20.0	13.6	66.4
1.5	53.3	45.2	25.0	10.1	64.9
2.0	48.6	49.4	30.0	7.1	62.9
2.5	44.9	52.6	34.6	5.0	60.4
3.0	41.6	55.4	37.4	4.0	58.8
4.0	36.8	59.2	41.0	3.0	56.0
5.0	33.2	61.8	45.6	$^{2.0}$	52.4
7.0	28.1	64.9	48.8	1.5	49.7
10.0	23.0	67.0	53.5	1.0	45.5
13.0	19.4	67.6 (max.)	61.0	0.5	38.5

Duplicate determinations were made on all runs at 0° and 20°, but not at 30°. The results of the duplicates checked very well with one another in every case. The data are given in Tables I, II and III. The data in Table II are shown diagrammatically in Fig. 2. The curves plotted from



the data in the other two tables are almost identical with the one in Fig. 2. The results in the tables are interpolated graphically to even percentages of water or toluene.

If the solubility surface in the composition temperature prism be drawn from the data of the three isotherms, it will be found that this surface rises abruptly from isotherm to isotherm. Temperature, therefore, has but little effect on the mutual solubility of the three components.

Attempts have been made by numerous authors to obtain mathematical expression for these curves, but with only moderate success. If the

¹ Bonner, J. Phys. Chem., 14, 738 (1910).

ı i

mounts of the two immiscible li ds soluble in a fixed am consolute liquid are plotted against each other, a curve is seo

n h

TABLE II

Data for Equilibrium Line between the One-Liquid Phase and Two-Liquid Phase Systems at 20°

% Water	% Toluene	% Acetone	% Water	% Toluene	% Acetone
0.5	76.0	23.5	15.0	19.0	66.0
1.0	68.9	33.1	20.0	14.9	65.1
1.5	58.5	40.0	25.0	11.5	63.5
2.0	53.6	44.4	30.0	8.5	61.5
2.5	49.4	48.1	35.0	6.0	59.0
3.0	45.9	51.1	37.6	5.0	57.4
4.0	40.6	55.4	40.5	4.0	55.5
5.0	36.6	58.4	43.8	3.0	53.2
7.0	30.6	62.4	48.3	2.0	49.7
10.0	25.0	65.0	52.1	1.5	46.4
14.2	19.8	66.0 (max.)	57.0	1.0	42.0
			65.2	0.5	34.3

TABLE III

DATA FOR EQUILIBRIUM LINE BETWEEN THE ONE-LIQUID PHASE AND TWO-LIQUID PHASE SYSTEMS AT 30°

% Water	% Toluene	% Acetone	$_{ m Water}^{ m \%}$	% Toluene	% Acetone
1.5	61.5	37.0	25.0	12.2	62.8
2.0	56.1	41.9	28.7	10.0	61.3
2.5	51.6	45.9	34.3	7.0	58.7
3.0	48.5	48.5	39.0	5.0	56.0
4.0	43.1	52.9	42.1	4.0	53.9
5.0	38.6	56.4	46.0	3.0	51.0
7.0	32.3	60.7	50.8	2.0	47.2
10.0	26.0	64.0	54.4	1.5	44.1
15.0	19.7	65.3	59.4	1.0	39.6
14.6	20.1	65.3 (max.)	68.3	0.5	31.2
20.0	15.5	64.5	71.5	0.4	28.1

can be fairly well expressed by the equation, $xy^n = \text{const.}$, in which x is the amount of one liquid, y the amount of the other and n a constant, depending upon the system and the temperature. This expression, however, is by no means exact. If we write the equation in logarithmic form, we have $\log x + n \log y = \log \text{const.}$ Differentiating we find, d $\log x + n \log y = 0$; or,

$$\frac{\mathrm{d}\,\log\,x}{\mathrm{d}\,\log\,y} = -\,n$$

Plotting $\log x$ against $\log y$ should give a straight line, if n is a constant. As a matter of fact, for this system the line is distinctly curved. Plotting y as the amounts of toluene and x as the amounts of water for a given weight of acetone, the curve is concave toward the $\log x$ axis. Other formulas have been suggested but none of them fits the curves satisfactorily.

Summary

- 1. The isotherm curves for the system, water-toluene-acetone, have been experimentally determined at three temperatures, 0°, 20° and 30°. An apparatus suitable for such determinations is described.
- 2. Temperature has but little effect on the mutual solubility of the three components.

MADISON, WISCONSIN

[Contribution from the Chemical Laboratory of Clark University, No. I, 30]

EQUILIBRIA IN SYSTEMS INVOLVING CALCIUM, HYDROGEN AND NITROGEN

By Charles A. Kraus and Charles B. Hurd Received July 26, 1923

The reactions of the more electropositive elements with hydrogen and with nitrogen and the interaction between the corresponding hydrides and nitrides, as well as the interaction of these compounds with nitrogen and hydrogen, possess considerable interest from the standpoint of the chemistry of nitrogen compounds. Up to the present time the available data are extremely meager. The present investigation was undertaken for the purpose of supplying further data in this field.

1. Action of Ammonia on Calcium and Barium Nitrides

Among the more recent and important investigations may be mentioned that of Mentrel,¹ who studied the reaction, $Ba(NH_2)_2 = Ba_3N_2 + 4NH_3$. He states that this reaction is reversible.

As is well known, calcium amide loses ammonia at higher temperatures and is ultimately converted to the nitride. Experiments were accordingly carried out in which the nitride was subjected to the action of ammonia in order to determine whether this reaction was reversible in the case of calcium.

Calcium amide was first prepared by treating the metal with liquid ammonia in a quartz tube in the presence of a trace of iron oxide, which served as catalyst. After vaporization of the excess ammonia, the resulting hexammoniate² was converted to the amide at temperatures slightly above that of the surroundings. The tube containing the amide was connected with a manometer, a vacuum pump, and a source of pure ammonia vapor. In a series of experiments, extending over a period of two months and at temperatures ranging from 200° to 850°, no indication of an equilibrium was observed. At higher temperatures, gradual decomposition of the amide took place with loss of ammonia and in the end there was left behind a yellow, porous material which consisted of calcium nitride.

¹ Mentrel, Compt. rend., 135, 740 (1902).

² Kraus, This Journal, 30, 653 (1908).

In view of the statement of Mentrel, the experiment was varied as follows. Ammonia was introduced into the system containing calcium nitride and measurements were made to determine whether any absorption took place either at a given temperature or on passing from higher to lower temperatures. In no case was such an effect observed.

To test these results further, metallic barium was treated in a similar manner. No indications of an equilibrium could be detected. Ammonia continued to be given off until only the nitride remained behind. On introducing ammonia gas into the tube containing the nitride, there was no indication of absorption at temperatures up to 850°.

Barium amide was also formed by passing ammonia over metallic barium. At 60°, a grayish deposit was observed on the surface of the metal which doubtless consisted of the amide. At 290°, this product melted, forming a dark gray liquid. At higher temperatures, this liquid became limpid and boiled vigorously, leaving behind a yellow solid. When this solid cooled, reliquefaction did not take place. This product was undoubtedly barium nitride. Experiments in which this nitride was treated with ammonia vapor gave no indications of reaction.

Our experiments, therefore, fail to confirm the observation of Mentrel and would appear to indicate that, under ordinary conditions, calcium and barium nitrides do not react with ammonia vapor.

2. Action of Nitrogen and Hydrogen on Calcium Hydride and Nitride, Respectively

Gautier³ studied the action of nitrogen on the hydrides of the metals of the alkaline earths and states that nitrogen may in part replace hydrogen in the hydrides at higher temperatures. Haber and van Oordt⁴ studied the action of nitrogen on calcium hydride and of hydrogen on calcium nitride. They state that the final product of the reaction of hydrogen on calcium nitride contains 15 parts of hydride per 100 parts of nitride, while the final product in the reaction of nitrogen with calcium hydride contains 10 parts of hydride per 100 parts of nitride.

Dafert and Miklanz⁵ have studied the action of hydrogen on the nitrides and nitrogen on the hydrides of the metals of the alkaline earths, as well as of mixtures of hydrogen and nitrogen on these substances. They have established the existence of compounds corresponding to the formula M₃N₂H₄, where M is an alkaline earth metal. The calcium and strontium compounds were obtained in a comparatively pure state. They established the formation of ammonia due to the action of hydrogen on barium nitride or, perhaps, Ba₃N₂H₄.

³ Gautier, Compt. rend., 134, 1108 (1902).

⁴ Haber and van Oordt, Z. anorg. Chem., 44, 340 (1905).

⁵ Dafert and Miklanz, Monatsh., 34, 1685 (1913).

Calcium hydride was prepared as follows. Calcium in the form of fresh filings was heated in a quartz tube through which purified hydrogen was passed. Reaction was found to take place readily at slightly elevated temperatures. The product first formed appeared somewhat yellow in color and was very brittle. This product was slightly grayish within, due, presumably, to the presence of a small amount of unchanged calcium, as was later confirmed by analysis. The initial product was pulverized and again treated with hydrogen, until a uniformly white product was obtained. This material contained a small amount of calcium oxide which, however, took no part in any subsequent reactions in which the hydride was involved. By rapidly handling it in a dry atmosphere the formation of oxide may be greatly reduced.

When nitrogen was passed over the hydride thus obtained, a gain in weight took place. The gain, however, was never found to be equal to the theoretical gain if complete conversion to nitride had taken place. This result was in part due to the fact that, at the temperature of the experiment calcium hydride is appreciably volatile as may be readily shown by heating calcium hydride in a stream of hydrogen.

In view of the uncertainty of the results derived from the weights of the substances involved in the reaction, analyses of the initial and final products were made. For this purpose a special apparatus was devised by means of which the product could be introduced into acidulated water and the amount of hydrogen evolved determined volumetrically.

The analyses of the original calcium hydride formed showed that this product contained over 90% of calcium hydride, CaH_2 . The remainder consisted chiefly of calcium oxide, due to the contact of the material with air. When this material was treated with nitrogen, the resulting product was found to contain less than 10% of calcium hydride.

On passing nitrogen over heated calcium, a product was obtained containing less than 6% of unchanged calcium. This material, heated to a very high temperature in hydrogen, increased in content of calcium hydride up to about 16%. Little increase above this percentage could be obtained. The temperatures required were in the neighborhood of 900°, under which conditions calcium hydride is comparatively volatile. At temperatures below 700°, calcium nitride, heated in hydrogen, gained in weight, probably due to the formation of an amide or imide.

3. Equilibrium in the System, Calcium Hydride, Calcium, Hydrogen

Measurements on this equilibrium were first carried out by Moldenhauer and Roll-Hansen⁶ who measured the equilibrium pressure of calcium hydride up to 1000° . They concluded that dissociation takes place in two stages according to the equations $CaH_2 = CaH + \frac{1}{2}H_2$, and CaH

⁶ Moldenhauer and Roll-Hausen, Z. anorg. Chem., 82, 130 (1913).

= $Ca + {}^{1}/{}_{2}H_{2}$. According to their determinations of the dissociation pressure of the sub-hydride, the equilibrium pressure is approximately ${}^{1}/{}_{2}$ that of the normal hydride. The above equilibrium was measured by Brönsted⁷ at lower temperatures and pressures. More recently the same equilibrium has been studied by Ephraim and Michel⁸ who virtually repeated the experiments of Moldenhauer and Roll-Hansen with somewhat divergent results. These earlier measurements will be discussed below.

Method and Procedure.—In view of the fact that the true equilibrium in this system may be obscured by certain sources of error, the method

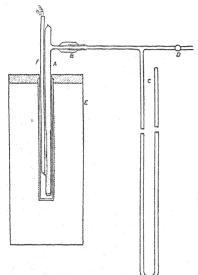


Fig. 1.—Apparatus employed in determining the dissociation pressure of calcium hydride

employed and the precautions observed will be described below in some detail.

The hydride was prepared from fresh filings of metallic calcium which were placed in a fused quartz boat in a horizontal Vitreosil tube, which was heated by means of a blast lamp. Pure, dry hydrogen was passed through the tube until tests showed that all air was displaced. The material in the boat was then heated to a moderate red heat, the current of hydrogen being regulated to compensate for the rapid absorption of gas which takes place under these conditions.

If calcium hydride, and to a lesser extent calcium itself, is heated to redness in contact with quartz, a certain amount of reaction takes place between the metal and the silica, wherein calcium oxide and silicon are formed. The reaction prod-

ucts, however, adhere to the walls of the silica boat and, if care is observed to remove the products without disturbing this coat, a pure calcium hydride may be obtained. From the silica boat the calcium hydride was transferred immediately into the measuring apparatus in which the equilibrium pressure of the hydride was determined.

The apparatus employed is shown in outline in Fig. 1.

The hydride was contained in a fused quartz tube A, of approximately 13 mm. internal diameter and 42 cm. length, closed at the bottom by means of a thick plug of fused quartz. The equilibrium chamber was joined to the remainder of the apparatus (constructed of glass) by means of a joint of de Khotinsky cement B.

At C is shown the manometer of the vacuum type. This manometer was checked from time to time against a high vacuum. Connection between the measuring system

⁷ Brönsted, Z. Elektrochem., 20, 81 (1914).

⁸ Ephraim and Michel, Helvetica Chim. Acta, 4, 907 (1921).

and the vacuum pump was made by means of the stopcock D. The equilibrium tube A was heated by means of an electric furnace E.

The temperature was measured by means of a platimum-platimum rhodium thermocouple F. The junction of the thermocouple was placed immediately against the quartz tube A at the point where the reacting material was located. The couple was calibrated before the experiments, by means of standard samples of lead, aluminum and copper, and at the end of the experiments it was checked against aluminum and found to have remained constant. The upper end of the furnace was closed by means of a plug of asbestos wool in order to minimize circulation. The temperature at different points within the furnace varied by less than 5°. All temperatures given were measured at the level at which the material was located in the quartz tube. The temperature was maintained constant by means of hand adjustment and ammeter control to within 1° between 600° and 1000°.

The greatest difficulty to be overcome in experiments with calcium hydride in quartz containers is due to the volatility of calcium hydride and its action on the quartz. Since hydrogen is evolved in this reaction, no determination of the equilibrium pressure can be made if the hydride is allowed to come in contact with the quartz container. This difficulty was somewhat troublesome in the earlier experiments and was finally overcome by placing the hydride in a tube constructed of pure iron and contained within the quartz tube A. The iron tube was of sufficient length to prevent the vapor of calcium hydride from coming in contact with the walls of the quartz tube.

The method of carrying out a series of experiments was as follows. Calcium hydride, prepared as described, was quickly mixed with about 1/2 its weight of fresh calcium filings, and placed in the iron tube. This tube was then allowed to slide to the bottom of the quartz tube A, the open upper end of which was then sealed off. The reaction tube was then quickly joined to the manometer system and immediately evacuated. By working rapidly and on days when the humidity was low, little change occurred in the hydride due to the action of moisture.

After exhausting the equilibrium chamber, the electric furnace was placed in position around the quartz tube, the thermocouple was introduced, and the furnace opening was plugged with asbestos wool. The temperature was then raised to approximately 800°, the system remaining attached to the pump. In this way any adsorbed gases were driven off. It was found that a certain amount of hydrogen was always evolved from calcium hydride made as above described, when heated to a temperature of from 300° to 400°. At higher temperatures this excess of hydrogen was reabsorbed by the excess of calcium present.

When all foreign gases had been removed from the system, the furnace was heated to about 970° and the temperature maintained constant. The pressure was then read at intervals until it reached constant value. A small amount of hydrogen was then withdrawn from the system by means of the vacuum pump and pressure readings were again taken until a constant value was reached. In this way equilibrium was approached from both sides.

After carrying out the measurement at a given temperature, the temperature was lowered and again maintained constant and pressure observations were made as before. This procedure was followed until a temperature was reached at which the rate of reaction was so low that measurements could not be made. The rate at which equilibrium is established varies greatly with the temperature. At 900° it was established in about 10 minutes, while at 600° approximately 10 hours was required.

Data.—The results of three independent series of measurements are given in the following table in which are given the temperatures at which

TABLE I

DISSOCIATION PRESSURE OF CALCIUM HYDRIDE AT DIFFERENT TEMPERATURES

CIVITACIA	X MINOCOLIA O	r. Chileron	TI I DICIDIA 111	20 11 2 14161411	T TAILT TAICTE
Seri	es 1	Seri	es 2	Seri	es 3
t°C.	$P_{\mathrm{em.\ Hg}}$	t°C.	$P_{\mathbf{cm}}$. $\Pi_{\mathbf{g}}$	t °C.	$P_{ m em}$. Hg
985	57.50	934.7	23.41	978.8	44.08
921	18.26	905.4	14.08	958.2	33.14
892	10.80	864.3	6.79	931.5	22.36
		834	3.76	871.2	8.40
		792	1.52	843.6	4.82
				769.2	0.93
				734.0	0.42

the pressure observations were made and the equilibrium pressures in centimeters of mercury as observed.

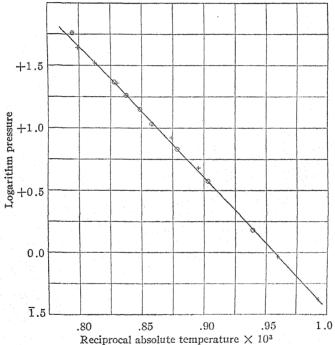


Fig. 2.—The dissociation pressure of calcium hydride as a function of the temperature

The results are shown graphically in Fig. 2, in which values of the logarithms of the pressures are plotted as ordinates against values of the reciprocals of the absolute temperature as abscissas.⁹ Points of Series 1

 9 The tangent to this curve at any point gives the value of H/R, where H is the energy change accompanying the reaction and R is the gas constant. If we write $\theta=1/T$, the reciprocal of the absolute temperature, then the differential equation of the curve is $\frac{\mathrm{d} \log K_p}{\mathrm{d} \Theta}=-\frac{H}{R}$.

are represented by combined crosses and circles, Series 2 by circles, and Series 3 by crosses. It will be observed that the points lie near a curve which closely approximates a straight line.

Discussion.—Assuming that hydrogen is the only constituent present in the reaction mixture whose pressure is appreciable, the pressure of the equilibrium mixture may be taken as a measure of the equilibrium constant. This assumption appears justified since no appreciable volatilization of materials was found to occur during the course of the experiments. Since the necessary thermal data for calculating the equilibrium constant at various temperatures are not known, the results obtained may be treated empirically. The best curve that may be drawn through the points deviates from a straight line by less than 1%.

Writing $\log P_{\rm H_2} = \frac{A}{T} + D$, where A and D are constants, and solving this equation for the values of the constants according to the curve, there is obtained the equation, $\log P_{\rm cm.} = -\frac{10.66 \times 10^3}{T} + 10.14$. This yields for the energy change accompanying the reaction the value 48400 calories.

Guntz and Bassett¹⁰ have determined the heat of formation of calcium hydride from its elements at ordinary temperatures and found it to be 46200 calories. Brönsted has also determined this quantity and obtained the value 45100 calories. The agreement of these values with that obtained from the curve cannot be looked upon as confirming the correctness of the results, since it is very doubtful that calcium hydride dissociates into hydrogen and metallic calcium. This is indicated, in the first place, by the results of Moldenhauer and Roll-Hansen, although their work is not altogether conclusive. Our own experiments would appear to indicate that metallic calcium could scarcely have been present in these experiments, since, according to Pilling, ¹¹ the vapor pressure of calcium is 0.173 mm. at 700° and 2.0 mm. at 805°, the melting point of calcium, while the boiling point lies at 1240°. With values of the vapor pressure of calcium of this order of magnitude, it is inconceivable that consistent measurements could have been obtained at temperatures approaching 1000°. ¹²

The determinations include three points at temperatures below the melting point of metallic calcium. The curve as drawn passes through these points and it does not appear that the precision of the measurements is

¹⁰ Guntz and Bassett, Compt. rend., 140, 863 (1905).

¹¹ Pilling, Phys. Rev., [2] 18, 362 (1921).

¹² This problem has been further studied by Mr. W. C. Johnson in this Laboratory. The volatility of calcium at temperatures in the neighborhood of 800° was confirmed. Furthermore, unquestioned evidence of the formation of a sub-hydride was obtained. While the normal hydride is white, the sub-hydride is dark gray to black in appearance. It appears to be much less volatile than calcium itself. The details of this work will be published later.

such as to warrant drawing the curve with an inflection point at the melting point. Nevertheless, it would be possible to draw a curve through the points for liquid calcium, which might be in somewhat better agreement with the determinations, by slightly reducing the slope of the curve at the higher temperatures.

The consistency of the results obtained in three independent determinations would appear to indicate that a true equilibrium exists in which calcium hydride and hydrogen are involved. While further evidence is desirable regarding the second solid phase present in the system, there can be little doubt that a sub-hydride exists as Moldenhauer and Roll-Hansen have suggested.

Our results are compared with those of earlier investigators in Fig. 4, in which the upper continuous straight line represents the results of this investigation and is identical with that of Fig. 2. The points determined by Moldenhauer and Roll-Hansen are represented by crosses, those determined by Ephraim and Michel by squares, while a few of the determinations of Brönsted are represented by double circles. The points represented by combined cross and circle, through which a broken line is drawn, represent Moldenhauer and Roll-Hansen's determinations of the sub-hydride equilibrium.

It will be seen that the determinations of Moldenhauer and Roll-Hansen are subject to very large variations. The lowest point falls very nearly on our curve, while at intermediate temperatures the points lie much above our curve. At higher temperatures the curve determined by these investigators again crosses our own and at the highest temperatures lies considerably below it. The determinations of Ephraim and Michel are inconsistent with both our own determinations and those of Moldenhauer and Roll-Hansen. The values determined by Brönsted lie considerably above our curve. An examination of Brönsted's data shows that his curve is markedly concave toward the axis of reciprocal temperatures, indicating, if the results are correct, that the energy change accompanying the formation of the hydride from its elements, or from a lower hydride, diminishes markedly with increasing temperature. Brönsted has proposed an equation for the curve which accounts for his values very satisfactorily on the assumption that, as he states, the sum of the heat capacities of calcium and hydrogen is 4.2 calories greater than that of the hydride. This, however, would correspond to an increase and not a decrease in the value of the energy change with increasing temperature. To account for a decrease, it would be necessary to assume that the heat capacity of the hydride is greater than that of the sum of the constituents from which it is formed, which assumption does not appear probable. As Lewis and Randall have pointed out,13 at higher temperatures, the difference in the

¹³ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., N. Y., 1923, p. 472.

heat capacities is probably very small, and it is not to be expected that the curve will deviate from a straight line sufficiently to become observable over a temperature interval of a few hundred degrees. Probably the form of the curve as found by Brönsted is due to undetermined sources of experimental error.

The broken line passing through the points represented by combined cross and circle represents Moldenhauer and Roll-Hansen's determinations of the equilibrium pressure of the sub-hydride. While these points lie consistently on a straight line, the curve passing through the points intersects our curve for the dissociation of the normal hydride and would also intersect a curve drawn through the points determined by Moldenhauer and Roll-Hansen for the same equilibrium. This throws doubt on the interpretation of the observed results. Subsequent measurements in this Laboratory, referred to in a preceding footnote, indicate that the dissociation pressure of the sub-hydride is exceedingly low, if measurable, at a temperature of 790°. While a sub-hydride in all probability exists, it must be assumed that any measurements of its dissociation pressure cannot be relied upon at the present time. Metallic calcium is so volatile at the temperatures in question that erroneous results may easily be obtained, due to the fact that the metal distils from the hotter to the cooler portions of the tube, under which conditions the normal hydride may conceivably be formed, yielding pressures commensurable with, but lower than those of the normal hydride at the true temperature.

4. Equilibrium in the System, Calcium Nitride, Calcium, Nitrogen

The nitrides of the metals of the alkaline earths possess a much greater stability than the corresponding hydrides. The formation of the nitrides through the action of nitrogen on the metals, however, takes place much less readily than does the corresponding formation of the hydrides. Moissan¹⁴ has studied the formation of nitrides from the elements, as well as the rate of formation and the influence of impurities.

The formation of barium nitride from barium and ammonia with the intermediate formation of barium amide has been studied by Mentrel. He showed that the nitride vaporizes appreciably at 1000°, but apparently exhibits no marked dissociation at that temperature. He also determined the heat of formation of barium nitride. Gautier³ has observed that the nitrides of barium, calcium, and strontium are dissociated to a much smaller extent than are the corresponding hydrides.

The heat of formation of calcium nitride has been determined by Guntz and Bassett, ¹⁰ who obtained the value 112,200 calories per mole. This is comparable with the heat of formation of some of the more stable com-

¹⁴ Moissan, Compt. rend., 127, 496 (1898); Ann. chim. phys., 18, 289 (1899).

¹⁵ Mentrel, Dissertation, Nancy, 1902; Chem. Zentr., 1903, I, 276.

pounds of calcium, and indicates that the stability of the nitride is relatively high.

In addition to the above-mentioned methods of preparing the nitrides, some others, less common, have been employed. Thus Ellis¹⁶ heated the oxide of the metal with magnesium in an atmosphere of nitrogen, while Wolk¹⁷ heated barium amalgam in nitrogen.

The formations of the nitrides of barium, strontium and calcium have also been studied by Dafert and Miklanz.⁵

Previous investigations have indicated that the nitrides are extremely stable substances, but no data are available as to the temperature at which the dissociation pressure might become appreciable. In view of the volatility of the nitrides, as well as of the metals themselves, it appeared impracticable to study these systems at temperatures much above 1000°, and accordingly little hope was entertained that accurate measurements might be obtained on the dissociation pressure of the nitrides. Nevertheless, it appeared of interest to study the order of magnitude of the dissociation pressures in these regions if possible.

Method and Apparatus.—The apparatus at first employed was similar to that used in the determination of the dissociation pressure of calcium hydride, shown in Fig. 1.

Calcium nitride, prepared from calcium filings, was mixed with about half its weight of fresh calcium filings and placed in an iron tube which was introduced into the quartz tube A. Although this was heated to over 1000° , no pressure could be observed on an ordinary vacuum manometer. The apparatus was accordingly modified so that the pressures could be read by means of a sensitive McLeod gage. With this gage, pressures could be accurately read between 0.1 and 0.001 cm. of mercury, and lower pressures could be approximated within 1×10^{-5} to 5×10^{-5} cm., depending upon the value of the pressure.

It was soon found, with the use of this gage, that the apparatus employed was not sufficiently tight to maintain the necessary high vacua. Accordingly, a mercury trap was introduced into the system between the apparatus and the stopcock connecting the apparatus with the vacuum pump. This trap was constructed in the form of a Y, the lower branch of which was connected with a mercury reservoir, by the elevation of which the connection between the apparatus and the stopcock could be closed.

It was found, as a result of experiment, that the tube A, which had originally been constructed of Vitreosil, was not sufficiently tight to permit accurate measurements to be made. Accordingly, it was replaced by a tube constructed of clear quartz. With this alteration, the system remained sufficiently tight to allow such measurements to be made. In the course of 72 hours, the pressure change observed amounted to 8×10^{-5} cm. The residual pressure in the system was measured before and after each series of observations at a temperature of 850°. The following values were obtained; before the first series, 6×10^{-5} cm.; between the first and second, 7×10^{-5} cm.; between the second and third, 8×10^{-5} cm.; and at the end of the third, 11×10^{-5} cm. The last pressure was measured at 950°. It was assumed that the true pressure of the nitrogen could be obtained by subtracting the pressure of the residual gases from the observed

¹⁶ Ellis, Chem. Zentr., 1909, I, 900.

¹⁷ Wolk, ibid., 1910, II, 1442.

total pressure. In general, the final rather than the initial pressure was assumed to give more nearly the correct value.

In carrying out a series of measurements, the furnace was slowly brought to a temperature of 1050°, and then allowed to cool slowly. The temperature and pressure were read at intervals. It was observed, during the first series, that a small amount of calcium had distilled into a region slightly above the point where the quartz tube extended out of the furnace. It was impossible to avoid this difficulty, but by working as indicated the effect was minimized as much as possible. The distillation of the calcium or some other product from the warmer to the cooler portion of the tube, however, may have had an appreciable influence on the measurements, since the equilibrium as measured may not have been that of the hottest portion of the tube, where the temperature was read. In the initial experiments, where the distillation process had not proceeded far, this factor was perhaps of little influence; but in succeeding experiments with the same sample of material the pressures as measured were doubtless somewhat lower than the true ones.

The results of three series of measurements made with the same sample are given in Table II. The results of the first run are undoubtedly more

Table II

Dissociation Pressure of Calcium Nitride

Series 1

		P	em. Hg X	104		$-P_{cm}$	н Х	104	
	t °C.	Obs.	Corr.	Calc.	t °C.	Obs.	Corr.	Calc.	
	958	1.0	0.3	0.23	1030	3.3	$^{2.6}$	2.95	
	969	1.0	0.3	0.36	1032	4.3	3.6	3.16	
	987	1.6	0.9	0.69	1033	3.7	3.0	3.27	
	1011	$^{2.2}$	1.5	1.56	1034	4.0	3.3	3.37	
	1012	2.5	1.8	1.62	1039	4.4	3.7	3.96	
	1014	2.7	2.0	1.73	1043	4.8	4.1	4.52	
	1019	2.9	2.2	2.05	1045	5.4	4.7	4.82	
	1020	2.8	2.1	2.12	1045	5.4	4.7	4.82	
	1020	2.8	2.1	2.12	1047	5.9	5.2	5.15	
	1022	3.0	2.3	2.27	1049	6.2	5.5	5.48	
	1028	3.6	2.9	2.77					
		Series	2 .			Serie	s 3		
t °C.	$P_{\rm em.} \times 10$	14 obs.	t °C.	$P_{\rm em.} \times 10^4$ obs.	t °C. Pem	, × 104 obs.	t °C.	$P_{\rm cm.} \times 10^4$	obs
965	0.9		1040	4.1	949	0.8	1046	4.1	
1016	2.4		1042	4.0	985	1.4	1042	3.9	
999	1.8		1040	3.9	1007	1.7	1037	3.1	
1020	2.5		1026	2.5	1020	2.4	1004	1.5	
1029	3.2		1007	2.0	1030	3.1	978	1.1	

reliable than the succeeding ones, in view of the distillation of the calcium from the hotter to the cooler portions of the tube, as just mentioned. In the first column is given the temperature on the centigrade scale and in the second column the observed pressure. In the third column, in the

first series of experiments, is given the observed pressure, corrected for the pressure of the residual gas, here assumed to be 7×10^{-5} cm.; and in the last column is given the calculated pressure according to an empirical equation.

If the logarithms of the pressures are plotted against the reciprocals of the absolute temperatures, the points should lie approximately on a straight line if the pressures measured represent true equilibrium pressures. When the observed pressures are plotted in this way, it is found that a curve results which is markedly convex toward the axis of reciprocal

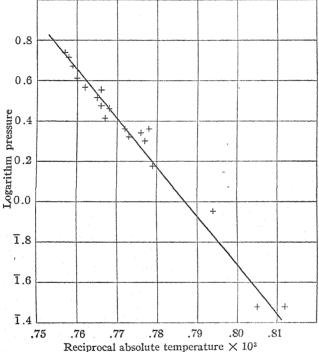


Fig. 3.—The dissociation pressure of calcium nitride as a function of the temperature

temperatures. When, however, the corrected pressures are similarly plotted, the points lie upon a straight line within the limits of the experimental error. The curves obtained for the three series of measurements do not coincide, although they run parallel with one another. Apparently, in succeeding experiments, the curves are displaced toward lower temperatures. This is doubtless due to the distillation of material from the hotter to the cooler portions of the tube, the temperature of the equilibrium mixture thus being lower than the temperature as measured.

In Fig. 3 the logarithms of the corrected pressures for the first series of

experiments are plotted as ordinates against the reciprocals of the absolute temperatures as abscissas. As may be seen from the plot, the points lie upon a straight line within the limits of the experimental error. The greatest deviations are observed at relatively low pressures, where the precision of the measurements is lowest. For the three points at the lowest pressures, the deviations reach a value of approximately 25%. For the remaining points, the deviations do not exceed 10% and for the most part are less than 5%. Considering the values of the pressures and the conditions under which the experiments were carried out, it would seem that, at the higher pressures and temperatures, the agreement is reasonably satisfactory. The straight line as drawn on the plot corresponds to the equation, log $P_{\text{cn}_L} = -\frac{24.36 \times 10^3}{T} + 15.166$. This yields for H, the energy change of the reaction per mole of nitrogen, the value 113,250 calories, which corresponds very closely with the heat of formation of calcium nitride as determined by Guntz and Bassett. It is doubtful, however, whether tais agreement can be looked upon as a confirmation of the results obtained, inasmuch as it is extremely doubtful that metallic calcium is here involved in the equilibrium. At the temperatures in question and with the low pressures existing in the apparatus, any free calcium present mus have vaporized into the cooler portions of the tube, probably to regions here the temperature would be little in excess of 700° or 70-50°. The fact hat a fairly good agreement is obtained among the different posints of given series would appear to indicate the existence of a definite equilibitum and it is possible that, in the case of calcium nitride, a sub-nitride myay be formed corresponding somewhat to the sub-hydride, as pointed out in the preceding section. In any case it may be concluded that realcium nitride is an extremely stable compound.

Equilibrium in the System Calcium, Hydrogen, Nitrogen, Calcium Nitride, Calcium Hydride, and Reaction Products

The results presented in Section 2 indicate that reaction takes place between hydrogen and calcium nitride and between nitrogen and calcium hydride. It was, therefore, decided to determine, if possible, whether equilibria exist in the system composed of calcium hydride, calcium, calcium nitride and hydrogen.

The apparatus employed was similar to that shown in Fig. 1, except that a side tube of quartz was connected to the tube A and provided with a small heating furnace. A palladium tube was introduced, closed at the end and sealed through a glass tube by means of a short length of platinum tubing. The end of the palladium tube was placed within 2.5 cm. of the tube A within the auxiliary furnace. The glass tube, into which the palladium tube was sealed, was connected with a manometer and a source of

hydrogen. When the palladium tube was heated by means of the auxiliary furnace, diffusion of hydrogen took place, either into or out of the system, depending upon the pressure. If any gas other than hydrogen were present in the reaction tube, its partial pressure could be determined by comparing the pressures indicated by the manometer connected to the reaction tube A and that attached to the palladium diffusion tube. Both the original reaction tube and the diffusion tube were provided with connections to sources of hydrogen and of vacuum.

A freshly prepared mixture of calcium hydride, calcium nitride, and calcium filings was introduced into an iron tube which was then sealed into the reaction tube A. The ingredients were quickly mixed before introduction into A and the subsequent operations were carried out as quickly as possible in order to minimize the influence of the atmosphere.

After introduction of the materials into the reaction tube the system was heated and pumped out, after which the equilibrium pressures were measured at a series of temperatures. The following values were obtained.

TABLE III

Dissociation Pressures in a Mixtur	E OF CALCI	um Hydridi	e, Nitride	and Calcium
<i>i</i> °C	1008.1	969.3	882.1	812.5
P cm. Hg	45.70	23.80	6.26	1.51

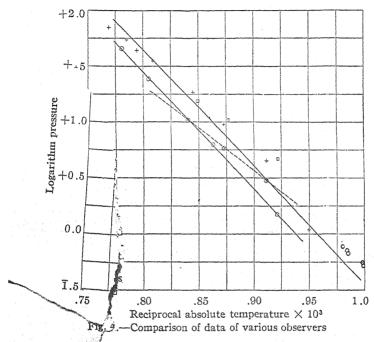
The gas present was evidently pure hydrogen, since the pressure readings on the two manometers were equal. Equilibrium was established very quickly and was approached from both sides, so that there can be no question but that the pressures read represented equilibrium pressures.

After the above series of readings had been made, the temperature was kept at 870° for several days and hydrogen was removed several times a day. After some days it was observed that the pressure was falling slowly from a value of 4 cm., although no hydrogen was being removed at the time. This continued until the pressure became so low that it could not be read on the manometers. When the temperature was raised to 1030°, no indication of evolution of gas was observed.

On readmitting hydrogen into the system through the palladium tube, rapid absorption took place. Unfortunately, it was found necessary to discontinue the investigation at this point.

The results are shown graphically in Fig. 4, in which the logarithms of the observed pressures are plotted as ordinates against the reciprocals of the absolute temperatures as abscissas. The points are represented as circles and a continuous straight line is drawn through them. The consistency of the values obtained would appear to indicate that a true equilibrium of some kind was measured. It will be noted that the curve is very nearly parallel with that of the calcium hydride equilibrium, which is represented by the upper continuous straight line. It is possible that a

portion of the calcium distilled from the hotter to the cooler portions of the tube and that the equilibrium represents the equilibrium of calcium hydride, the temperature being in error, due to the distillation effect. This would not, however, account for the rapid absorption of hydrogen in the later



stages of the experiment. Furthermore, a consistent series of pressure readings extending over a considerable period of time would not be expected under these conditions.

Summary

The action of ammonia on calcium and barium nitrides has been investigated. Contrary to the statement of Mentrel, no indications of absorption of ammonia by these nitrides could be observed.

Calcium hydride, treated with nitrogen, yields an end product containing less than 10% of hydrogen, and calcium nitride treated with hydrogen yields a product containing approximately 16% of hydrogen.

The dissociation pressure of calcium hydride has been measured at a series of temperatures. The results indicate the existence of a definite equilibrium involving hydrogen and calcium hydride. The third phase is uncertain, but the conditions of the experiment together with the observations of earlier investigators render it probable that a sub-hydride of calcium exists. The results obtained are compared with those of earlier investigators.

An attempt has been made to measure the dissociation pressure of calcium nitride at temperatures somewhat above 1000° . Reproducible pressure readings were obtained of the order of magnitude of $0.3\text{--}5.5 \times 10^{-4}$ cm. The results are consistent with an energy change accompanying the reaction of 113,250 calories, which agrees well with the heat of formation of calcium nitride at ordinary temperatures, as determined by Guntz and Bassett. It is pointed out that in all probability calcium could not have been present as a third phase in this equilibrium.

In a system consisting initially of a mixture of calcium, calcium nitride and calcium hydride, an equilibrium was found to exist at temperatures in the neighborhood of 1000°. Only hydrogen was present in the vapor phase. After continued heating at 870°, the hydrogen was ultimately completely absorbed.

Worcester, Massachusetts

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A PHOTOCHEMICAL STUDY OF ACETYL-CHLORO-AMINOBENZENE¹

By J. H. Mathews and R. V. Williamson Received July 26, 1923

In connection with a series of investigations which were being carried out in this Laboratory, there was needed a light sensitive compound whose changes could be easily and accurately followed. The compound, acetyl-chloro-aminobenzene, appeared to be one that might serve the purposes for which these compounds were wanted.

Blanksma² appears to be the first to have noted that the compound was sensitive to light and he stated, "The reaction is much accelerated by light and it appears to be a general rule that the radicals Br, Cl, NO₂, NO and O attached to nitrogen, change places, under the influence of sunlight, with an H atom in the nucleus."

Chattaway and Orton also made some velocity measurements on the transformation of the compound in sunlight.³ But there appears to have been no study made of the effect of light on the transformation of the compound under conditions such that the light intensity and conditions of the experiments were under control. Therefore, the present investigation was undertaken for the purpose of obtaining velocity measurements under conditions which could be duplicated.

¹ This paper constitutes the major part of a thesis submitted by R. V. Williamson in partial fulfilment of the requirements for the degree of Master of Science at the University of Wisconsin.

² Blanksma, J. Chem. Soc., 82, 646 (1902); Rec. trav. chim., 21, 290 (1902).

³ Chattaway and Orton, Proc. Chem. Soc., 18, 200 (1902).

The compound has attracted considerable attention in connection with the theory of solutions. With dil. hydrochloric acid the compounds R.CO.NR'Cl undergo a molecular rearrangement in which the chlorine attached to the nitrogen exchanges places with one of the hydrogen atoms of the benzene ring. This reaction may be represented as follows: CH_3 - $CONClC_6H_5 + HCl = CH_3CONHC_6H_4Cl + HCl$.

From this equation, it is apparent that the hydrochloric acid acts as a catalyst, as the only change in the substances present has been a molecular rearrangement of the acetyl-chloro-aminobenzene to chloro-acetanilide. The above reaction is a monomolecular reaction in the presence of dil. hydrochloric acid but does not follow the monomolecular equation at higher concentrations of acid. It follows the equation for a bimolecular reaction in the presence of hydrobromic acid. These data have led Acree, Senter⁵ and others to propose the "Dual Theory" of reaction in solution, that is, both ions and molecules react when a reaction takes place in solution.

Harned and Sethz have opposed this "Dual Theory" and have shown that the velocity of rearrangement of acetyl-chloro-aminobenzene to p-chloro-acetanilide by hydrochloric acid is proportional to the product of the hydrogen and chlorine ions.⁶

In view of the theoretical importance of the catalytic reactions which this compound unsergoes in the dark it may be of interest to present the data obtained in agard to its behavior under the influence of light from a quartz mercury—por lamp in different solvents and under various conditions.

Preparation and Purification of Chemicals Used

The acetyl-chloro-aminobenzene was prepared by Slosson's method. The melting point of the compound was 89°. All chemicals used were prepared by purification of the standard brands of c. p. materials.

Apparatus

A quartz mercury-vapor lamp of a common commercial type was used as the source of illumination. On each side of the lamp was placed a quartz flask for holding the solution to be examined. All flasks were of the same size and each flask was provided with a mechanical stirrer which operated from the same pulley so as to produce the same agitation in each flask. A thin sheet of water flowed from the constant-temperature reservoir over the surfaces of the flasks to maintain them at the desired temperature. The electrical circuit was provided with a variable resistance for controlling the current passing through the lamp. The apparatus was set up in a dark room and all the work connected with the experiments was done in the dark room, with the help of electric lights.

⁴ Acree and Johnson, Am. Chem. J., 37, 410 (1907); 38, 258 (1908).

⁵ Senter, J. Chem. Soc., 91, 467 (1907).

⁶ Harned and Seltz, This Journal, 44, 1475 (1922).

⁷ Slosson, Ber., 28, 3265 (1895).

Procedure

By trial experiments the exact position of the flasks, with respect to the light, necessary to produce duplicate results when portions of the same solution were placed in each flask was determined. The flasks were then marked and the necessary measurements made to allow them to be removed from their clamps and replaced in exactly the same positions. They were filled with definite amounts of the solution to be examined, the stirrers started, the water for controlling the temperature was turned on, a light shield inserted between the light and the flask and then the current was turned on the lamp. When the lamp had reached its maximum intensity, a sample of 2 cc. was removed from the 100cc. flask for the initial titration, and then the light shield was removed. At definite time intervals other samples were removed for titration. A check was always carried on at the same time, to determine the velocity of the dark reaction, by means of a similar flask painted with asphaltum varnish to protect the solution from the light. The velocities of the reactions of two different solutions were compared by placing one solution in Flask 1 and the other in Flask 2.

The course of the reaction was followed by titrating with sodium thiosulfate solution the iodine liberated when the sample was allowed to run into an excess of potassium iodide acidified with hydrochloric acid. The acetyl-chloro-aminobenzene liberates iodine from a potassium iodide solution acidified with hydrochloric acid, whereas the transformation product, p-chloro-acetanilide does not.

The temperature of the water flowing over the flat impound, acetylmeter and ammeter readings were recorded after each he purposes for following is a typical example of the method of recording shows the variation in temperature and voltage during an expension was

		TABLE I							
	TYPICAL DATA								
Time	Volts	Amps.	Temp.	Na ₂ S ₂ O ₂ Cc.					
9.25	67	3.0	21.0	8.70					
9.40	66	3.05	21.4	7.55					
9.55	65.5	3.1	20.9	6.45					
10.10	68	3.05	20.6	5.40					
10.25	68	3.1	20.6	4.28					
10.40	69.5	3.1	20.7	3.20					
10.55	65	3.1	20.9	2.35					
11.05	69	3.1	20.7	1.90					
11.15	69	3.1	20.6	1.40					
11.30	70	3.1	20.7	1.20					
11.40	68	3.1	20.9	1.10					

This is a fair example of the variation in voltage and temperature but the amperage is an average reading of the ammeter. The amperage remained constant for the most part at the point indicated, but occasionally showed temporary fluctuations of ± 0.2 ampere.

Three experiments are recorded below showing the velocity of the dark reaction when the compound was dissolved in dil. acetic acid, and the degree of accuracy obtainable when portions of the same solution were placed in each flask.

Expt. 1.—1.6950 g. of acetyl-chloro-aminobenzene was dissolved in 100 cc. of glacial acetic acid and diluted to 1 liter with distilled water. The solution was kept in a brown bottle which was placed in the ice chest with cracked ice surrounding it. We shall call this "Solution A." Samples of Solution A were titrated from time to time to get the velocity of transformation in the dark.

Time in min	0	21.60	42.90	55.38	69.24
$Na_2S_2O_3$, cc	19.77	19.64	19.49	19.33	19.13

Expt. 2.—Expts. 2 and 2' were made to show that the two flasks were so adjusted that the velocity of the reaction was the same when they contained portions of the same solution. The solution in this experiment was made by taking 90 cc. of Solution A and diluting it to 180 cc.

Temp. 3.01°. \ Volts 68.7.	Amps. :	3.0						
Time in min	0	44	96	137	206	292	340	617
Na ₂ S ₂ O ₃ , cc	9.85	8.10	6.57	5.50	3.98	2.52	2.00	0.25
Monomol. vel. const. \times 10 ³	•••	1.9	1.8	1.9	1.9	2.0	2.0	1.9

Expt. 2'.—This experiment is a duplicate of Expt. 2 except that the solution gas contained in the flask which was on the opposite side of the lamp.

Time in no.	0	45	97	163	217	300	341	617
Na ₂ S ₂ O ₃ , cc	9.85	8.00	6.45	4.78	3.64	2.29	1.85	0.29
Monomol. vel. const. × 103		2.0	1 9	1.9	2.0	2.1	2.2	2.0

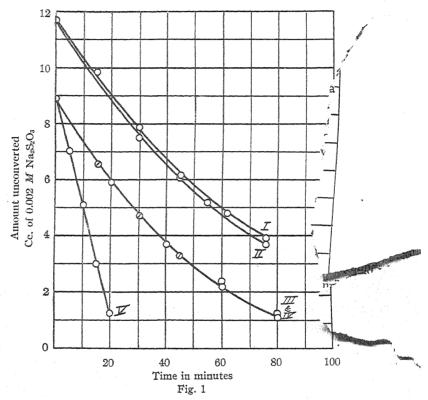
These experiments show that the reaction follows the equation for monomolecular reactions in dil. acetic acid solution under the influence of light, which is characteristic of photochemical reactions. When the compound was dissolved in other solvents, however, it was not always possible to calculate the velocity constant.

Experimental Part

In Fig. 1, Curves I and II compare graphically the velocities of reaction for two solutions of 0.01~M acetyl-chloro-aminobenzene in 10% acetic acid solution plus 2% sodium acetate and in 10% acetic acid alone, respectively, when exposed to ultra-violet light. The curves show that practically no effect was produced by the addition of the sodium acetate. The velocity constants calculated by the equation for monomolecular reactions were 0.0064 and 0.0067; the difference is within the experimental error.

Curves III and IV, Fig. 1, are duplicate determinations for the same strength, and under the same conditions as Curves I and II, except that benzene was used as the solvent.

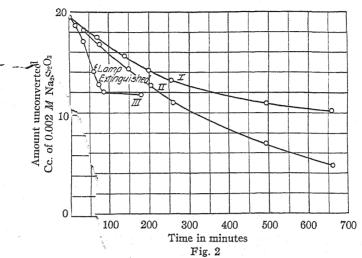
Curve V, Fig. 1, is a duplicate of Curves III and IV except that the benzene used as a solvent was recovered from the solutions used in producing Curves III and IV. The benzene was recovered by distilling it from the solute. Evidently some compound distilled with the benzene which catalyzed the reaction and speeded it up to a very marked degree. No effort was made to determine the exact reason for this behavior.



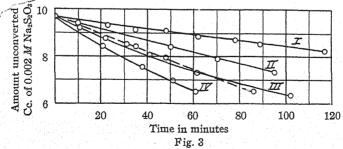
Curves I and II, Fig 2, show the relative transformation of a $0.01\ M$ and $0.02\ M$ solution in 10% acetic acid under the influence of light of the same intensity. While the stronger solution showed a slightly greater amount transformed in unit time, the velocity constant was only 0.0009 as compared with 0.0017 in the more dilute solution. That is, the velocity constant for the solution of double strength had a value of one-half that for the more dilute solution.

Curve III, Fig. 2, shows the comparative amount transformed when the solvent is glacial acetic acid as compared to 10% acetic acid in Curves I and II. It shows also that the reaction continues with practically no change in velocity when the light is extinguished. This solution in glacial acetic acid showed no change during a period of one-half hour previous

to turning on the light. However, when the light once initiated the reaction, it proceeded without diminution when the light was extinguished. This was found to be true in other solutions where water was absent.



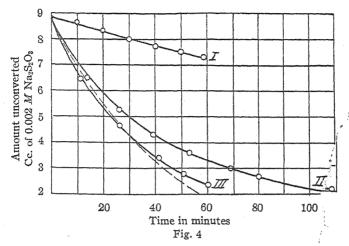
In view of the fact that hydrochloric acid catalyzes the transformation in the dark it was thought that perhaps the reaction would be extremely sensitive in the light in the presence of this acid. Curve I, Fig. 3, shows the mount of transformation of a 0.01 M solution in 10% acetic acid containing 45% N hydrochloric acid in the dark as compared with the light reaction in 10% acetic acid in Curve II, the light reaction in 10% acetic acid plus 25% of N hydrochloric acid in Curve III and to the light reaction of 10% acetic acid containing 45% of N acid in Curve IV. The broken line



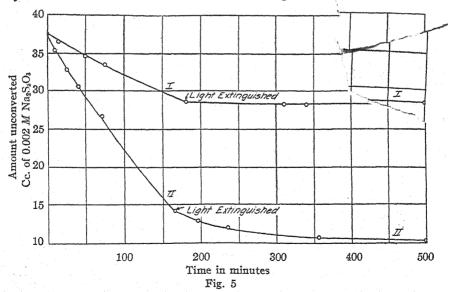
curve represents the sum of the dark reaction in the presence of 45% of N hydrochloric acid plus the light reaction in 10% acetic acid. This indicates that the light reaction in the presence of hydrochloric acid is greater than the sum of the light reaction in dil. acetic acid plus the dark reaction produced by hydrochloric acid.

Curve I, Fig. 4, shows the transformation in 10% acetic acid under the

action of light compared with the dark reaction in 10% acetic acid plus 2% of 0.25~N hydrobromic acid as shown in Curve II, and the light reaction



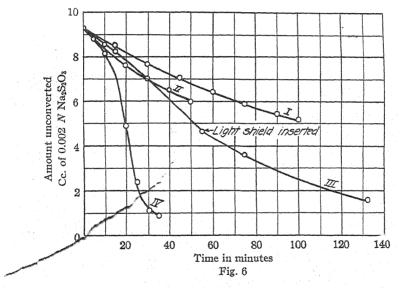
in 10% acetic acid plus 2% of 0.025~N hydrobromic acid, Curve III. The broken line represents the sum of the individual reactions represented by Curves I and II. From these results the light reaction in 10% acetic



acid solution containing 2% of 0.25~N hydrobromic acid is shown to be practically equal to the sum of the light reaction in 10% acetic acid plus the dark reaction produced by the presence of the hydrobromic acid in the 10% acetic acid solution.

Curve I, Fig. 5, shows the result of illuminating with ultra-violet light a 0.04~M solution of acetyl-chloro-aminobenzene in 10% acetic acid in comparison with a solution of the same strength in benzene as shown in Curve II. It is apparent that the acetic acid solution ceased to react as soon as the light was turned off but the reaction in the benzene solution proceeded slowly for some time after the light was extinguished. Concordant velocity constants were calculated for both the acetic acid and the benzene solutions. The velocity constant as calculated by the monomolecular equation was 0.0023 for the benzene solution and 0.00065 for the acetic acid solution.

Some experiments were carried out to determine the effect of concentration of the solute in benzene as solvent and results similar to those found in acetic acid were obtained, as shown in Curves I and II, Fig. 2.

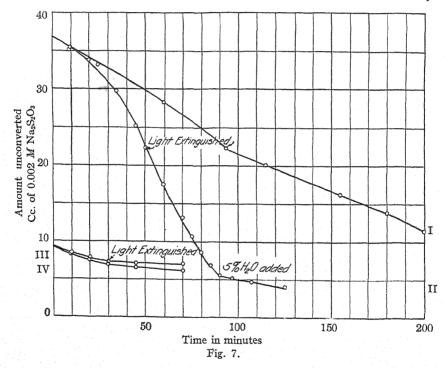


Curves I and II, Fig. 6, show the effect of temperature on the velocity of transformation of a 0.01 M solution in 95% alcohol. The temperature of the solution in Curve I was 0.7° and that in Curve II was 21.1°.

Curves III and IV show the effect of temperature on an absolute alcohol solution of $0.01\,M$ concentration. The temperature of the solution for Curve III was $0.3\,^{\circ}$ and for Curve IV was $21.2\,^{\circ}$. It will be noticed that the effect of temperature on the 95% alcohol solution is very much less marked than on the absolute alcohol solution. This is in accord with the usual low temperature coefficients of photochemical reactions. Dilute solutions of acetyl-chloro-aminobenzene in alcohol containing small amounts of water act like true photochemical reactions, as is shown in Fig. 7, Curve III, whereas in absolute alcohol solutions the reactions are

not true photochemical reactions, since the reaction proceeds without the light after the reaction is initiated, as is shown by Curves II and IV, Fig. 7. Therefore, the temperature coefficient of the reaction in absolute alcohol is equal to the coefficient for an ordinary chemical reaction.

In Fig. 7, the presence of small amounts of water is shown to have the effect of a negative catalyst. Curve II shows the velocity of transformation of a $0.04\,M$ solution in absolute alcohol with and without the light. No diminution whatever is noted when the light is extinguished after the reaction is initiated, but the addition of a small amount of water toward the end of the reaction causes a marked decrease in the velocity



of transformation. Curves III and IV show the effect of extinguishing the light when the solvent is 95% and partially dehydrated alcohol, respectively, and the concentration of the solute is only 0.01~M. Curves I and II show the results obtained with a stronger solution (0.04~M) in 95% and with partially dehydrated alcohol, respectively. The alcohol used in the solution for Curves II and IV was treated with anhydrous copper sulfate until only traces of water remained in the alcohol, but of course was not completely anhydrous. From these curves, it is seen that water retards the velocity of transformation, but its effect is reduced as the strength of the acetyl-chloro-aminobenzene is increased. For

example, the reaction stops completely in a $0.01\,M$ solution in 95% alcohol when the light is removed, as shown by Curve III, but is only slightly retarded when the concentration is increased to $0.04\,M$, as shown by Curve I.

Discussion of Results

Acetic Acid Solutions.—Others have shown that the transformation of acetyl-chloro-aminobenzene in dil. acetic acid solution is very slow in the absence of light. When hydrochloric or hydrobromic acid is added to the solution, however, the decomposition proceeds in the dark. With hydrochloric acid, the reaction is monomolecular, at least within certain limits of concentration, whereas with hydrobromic acid it is bimolecular. Our experiments show that a 0.01 M solution in 10% acetic acid containing 1% of 0.25 N hydrochloric acid showed no appreciable decomposition at the end of 3 hours. On the other hand, a solution containing 1% of hydrobromic acid in a 10% acetic acid solution of the same strength of acetyl-chloro-aminobenzene showed a marked decomposition. A higher concentration of hydrochloric acid, for example a solution containing 25% of N hydrochloric acid, produced rapid transformation in the dark. It appears from these experiments, therefore, that a certain concentration of hydrochloric acid is necessary before the transformation takes place.

The light reaction in 10 or 20% acetic acid appears to follow the equation for a monomolecular reaction, which is characteristic of photochemical reactions, but the velocity constant is not independent of the initial concentration of the solute, as is the case with monomolecular reactions. The velocity of the light reaction is the same whether the solution contains 10 or 20% acetic acid.

The sum of the velocities of the dark reaction with hydrobromic acid as catalyst plus the light reaction in 10% acetic acid is the same as for the light reaction in the case of a 10% acetic acid solution containing the same concentration of hydrobromic acid. The light reaction in the case of a 10% acetic acid solution containing hydrochloric acid as catalyst was somewhat greater than the sum of the light reaction in 10% acetic acid and the dark reaction with hydrochloric acid as catalyst.

In dilute acetic acid (10 or 20%) the transformation proceeds only under the influence of light but in a glacial acetic acid solution the reaction proceeds without the action of light after the reaction is started by the light.

Alcoholic Solutions.—Alcoholic solutions of acetyl-chloro-aminobenzene were found to behave similarly to those in acetic acid. $0.01\ M$ solutions in alcoholic solvent containing as much as 95% of alcohol appeared to give true photochemical reactions in that they proceeded only under the influence of light, showed a temperature coefficient of 1.23 and conformed to the equation for monomolecular reactions. The velocity constant was not independent of the concentration, however, but was only about half

as great when the concentration of solute was doubled, as was also the case in dil. acetic acid.

When the concentration of solute in 95% alcohol was increased to 0.04 M, however, the reaction ceased to be truly photochemical but continued after the light was extinguished, although at a diminished velocity.

In absolute alcohol the compound was stable in the dark but after the transformation was initiated by the light the reaction proceeded with undiminished velocity when the light was extinguished. The velocity was very much greater in the absence of water in both alcoholic and acetic acid solutions.

The temperature coefficient for the reaction in absolute alcohol was about 1.6 as compared with 1.23 for the reaction in dil. alcohol, which is characteristic of the difference between photochemical reactions and ordinary chemical reactions.

Benzene Solutions.—These experiments show that the velocity of transformation of acetyl-chloro-aminobenzene, when dissolved in benzene, under the influence of the light from a quartz mercury-vapor lamp, as well as the decomposition under the action of the light, is between that for dil. acetic acid and absolute alcohol solution. The velocity of the light reaction in benzene solution is about the same as in 95% alcohol. The velocity constants can be calculated for all concentrations tried by means of the equation for monomolecular reactions. The velocity constant is not independent of the concentration of the solute, however.

When the transformation is started in benzene solution by the action of light and the lamp is then extinguished, the reaction does not stop immediately as it does in 10% acetic acid solution of the same concentration nor does it continue without diminution as it does in an absolute alcohol solution, but the velocity decreases very rapidly for a short time and then very slowly.

Summary

The decomposition of acetyl-chloro-aminobenzene under the influence of the light from a quartz mercury-vapor lamp has been studied in various solvents. The solvent has been found to have a marked effect on the behavior of the reaction.

When water is added to an alcoholic or glacial acetic acid solution of acetyl-chloro-aminobenzene the velocity of the light reaction is greatly diminished. It also causes the reaction to proceed as a true photochemical reaction, whereas in the absence of water the reactions in absolute alcohol and glacial acetic acid solutions proceed without the action of light after the reaction is once initiated.

MADISON, WISCONSIN

[Communication from the Rare and Precious Metals Experiment Station of the Department of the Interior, Bureau of Mines, in Coöperation with the Mackay School of Mines, University of Nevada]

CHEMICAL ACTION PRODUCED BY RADON¹ III. THE DETERMINATION BY A CHEMICAL METHOD OF THE MEAN EFFECTIVE PATH OF ALPHA PARTICLES IN SMALL SPHERES²

By S. C. LIND AND D. C. BARDWELL RECEIVED JULY 27, 1923

1. In studying the relation between ionization and chemical reaction in gases containing radon, the ionization cannot be measured, but must be calculated from the quantity of radon and the mean path of the α particles in the gas being acted upon.³ The desirability of an exact knowledge of the mean path of the α particles is therefore apparent. The problem is simplified by using spherical reaction vessels. The mean path of all α particles projected (by radon) from all points within the sphere in all directions in straight lines until they strike the wall is $0.75 \times r$ (where r is the radius of a sphere). The mean path from all points on the inner surface (RaA and C) in all directions until the wall is again reached is $0.5 \times r$. But doubt exists as to the actual proportions of RaA and RaC that are on the wall when emitting α particles, which evidently would affect the length of path of the α particles emitted and hence the quantity of ionization. It appears impossible to settle this point with existing data on the rate of diffusion of active deposit; and while the direct determination can be made for RaC by means of its γ radiation, it is not possible for RaA. Saturation current methods of determining the ionization are also not applicable since the imposition of an electrical field would influence the deposition of active deposit.

The following indirect chemical method therefore appears to have promise, since it had already been shown by one of us³ that the rate of chemical combination of hydrogen and oxygen under the influence of radon mixed with them in spheres of different sizes is directly proportional to the radius of the sphere, and hence to the mean linear path of the α particles.

The proposed method based on the mean path principle is, in brief, to make a series of manometric measurements of the velocity of combination of electrolytic hydrogen and oxygen in the same sphere under two different

¹ The term *radon* is adopted for radium emanation, according to the recommendation of the International Committee on Chemical Elements. This Journal, **45**, 868 (1923).

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³ Lind (a) This Journal, 41, 547 (1919); (b) American Chemical Society Monograph No. 2, "Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., N. Y., 1921, p. 105.

conditions: (A) with the radon confined at the center of the reaction vessel in a minute α -ray bulb, which may be regarded provisionally as a point source of α radiation in all directions; (B) with the radon mixed in the reaction sphere with the hydrogen and oxygen. The sphere must, of course, be small enough for the α particles of shortest range to pass entirely across it in the given gases at the highest pressure employed.

In simplest terms, the velocity of chemical reaction in B will be proportional to the effective mean path of the α particles in the sphere, which

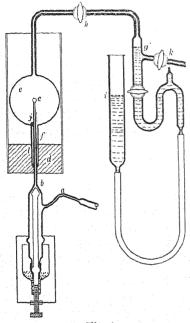


Fig. 1

is sought; while the velocity in A will be proportional to a path which must be the radius r itself. Therefore, the ratio chem. velocity (B) chem. velocity (A) represents a fraction of the radius which is the mean path sought in B. A number of corrections are to be applied which are considered later.

2. The Experimental Method.—The apparatus used for Method A is shown in Figs. 1 and 2. Radon was collected from a solution containing 220 mg. of radium element as 50% radium barium chloride, Ra(Ba)Cl. dissolved in 5% hydrochloric acid. The method used to obtain radon purer than is needed for therapeutic purposes has been previously described.⁴ The radon and residual gases must, after purification, occupy a volume not exceeding 1 to 2 cu. mm. at a pressure of 1 to 2 atmospheres. The elec-

trolytic mixture of hydrogen and oxygen (dry) is first introduced through the stopcocks k and h to give the desired pressure in e. The purified radon is then passed from the purification train (not shown) through the capillary tube a past a ground glass valve b. Finally b is closed so as to confine the radon in front of the mercury just at the neck of the α -ray bulb e. The ground glass valve e is adopted from Taylor, e

⁴ (a) Lind, Am. Chem. J., 47, 406 (1912); (b) Sitzb. Wien Akad., 120, IIa, 1714, (1911).

⁵ To minimize the danger of puncturing c (Fig. 2) by sparking through, as a result of the accumulation of unipolar charge, a very fine platinum wire (l) was sealed through the capillary wall between d and f making contact with the mercury in the capillary and continuing at the other end well up into e. A blank test showed that this small quantity of platinum does not catalyze measurably the combination of hydrogen and oxygen.

⁶ Taylor, This Journal, 37, 30 (1915).

but without his silica rod temperature compensator. By making the bore of the capillary between b and c and hence the volume of mercury very small, it was found that temperature compensation could be dispensed with over a range of 10° , which was two or three times the actual maximum fluctuation.

Owing to the difficulty of blowing an α -ray bulb on a very short capillary, it was found necessary to make the glass in-seal d at a greater distance from c than could be allowed for the radius of the reaction sphere e. Consequently a dead arm (for radiation but open to hydrogen and oxygen) occurs in the annular space along f. Attempts to fill in f with inert material failed; mercury has the disadvantage of contributing vapor to e so that a deposit of oxide formed on c, owing to the oxidizing conditions in the intense ionization region around it, resulting in a prohibitive increase of stopping power of e for e rays. Attempts to fill in e with fused salt also failed, because the salt (cutectic mixture of lead chloride and silver chloride) upon solidifying broke the thin capillary. The dead arm had, therefore, to be filled with the electrolytic gas, which introduces a correction that will be treated subsequently.

In the reaction sphere e small areas of a mixture of potassium and sodium oxides were fused flat upon the wall in two or three places for desiccation. The manometric measurements of the course of the reaction were made by reading at g, separated from e by a 0.5mm. capillary 10 cm. long and by a stopcock h to prevent diffusion of mercury vapor into e. Except at the time of readings the mercury level is raised into the capillary. The mercury levels at g and in the leveling bulb at i were read with a cathetometer without

Fig. 2

detaching from the apparatus so as to avoid disturbing the mercury setting at c which is very delicate.

The procedure B is identical with A just described except that in B the radon is allowed to mix with the hydrogen + oxygen in e by breaking c. This is accomplished (after Procedure A has been followed for 2 or 3 days so as to obtain a good set of velocity constants) by lifting the "magnetic capsule" j with an electro-magnet and allowing it to fall against c which is readily crushed owing to its extreme thinness (about 0.0025 mm.). This "magnetic capsule" is merely a soft iron pin (3 mm. long and 2 mm. in diameter) enclosed in a glass shell of total volume 0.2 cc. In method B the dead arm f is then filled with mercury (from the manometer) exactly up to the shoulder, thus making the reaction vessel e a perfect sphere.

The general procedure just described not only furnishes a convenient method of continuing B from A with the same radon and the same elec-

 $^{^{7}}$ Use of a liquid-air trap to stop mercury vapor during the short reading intervals when h is open was found unnecessary.

trolytic gas, but also possesses the great advantage of making the comparison of the two velocities independent of any γ -ray measurement of the quantity of radon (which is the same in both cases, taking into account, of course, the decay factor).⁸

The pumps used for evacuation were a mercury vapor diffusion pump of Pyrex glass backed up by a Gaede rotary oil pump. A vacuum of 10^{-5} mm. (neglecting mercury vapor) was attained in the system before the purification and introduction of radon was begun.

The manometric measurements were never begun until radon had been in place for 4 hours to insure equilibrium with and definite position of RaA and RaC. The initial pressure P_0 , and E_0 the initial quantity of radon refer, of course, to the same zero time t_0 .

3. Experimental Results and Calculations.—For the sake of confirmation, two independent experiments were made using reaction spheres of different diameters and α -ray bulbs of slightly different dimensions. In Table I the dimensions of both are given. The factors primarily controlling the velocity are the quantity of radon present, the pressure of the reacting gases, and the dimensions of the reaction vessels. The other

 $T_{ABLE} \; I$ Dimensions of Reaction Spheres and of $\alpha\textsc{-Ray}$ Bulbs for Expts. 1 and 2

	Reaction sphere			cr-Ray bulb9			
	Diameter Cm.	Volume Cc.	Vol. of dead arm Cc.	bulb Cm.	-Diameter o neck Cm.	tip Cm.	Wall thickness Cm.
Expt. 1	3.563	23.69	1.16	0.159	0.063	0.042	0.00025
Expt. 2	4.259	40.46	1.07	.145	.047	.046	.00025

 $^{^8}$ γ -Ray measurements of the radon were made in order to give an absolute value to the velocity constants reported, but they are not regarded as very accurate because in passing radon over the ground-glass valve b some of it invariably was trapped by the rough surfaces. This rendered heavy screening of b necessary during the subsequent γ -ray measurement, thus introducing uncertainties not arising in the ordinary γ -ray measurement of Rn.

⁹ The measurements of the bulb, neck and tip were made by means of a calibrated micrometer eye-piece (1 div. = 0.00234 cm.); those of the wall thickness by viewing the edge of the broken wall (1 div. = 0.000124 cm.). A preliminary measurement of the wall thickness to determine before use, the suitability of each bulb, was made radiometrically by means of a zinc sulfide screen after introducing radon.¹0 The value obtained for wall thickness by the radiometric method was about twice as great as that by the microscopic method. The discrepancy is probably ascribable to the failure of the screen to render α-rays visible at the extreme ends of their paths. Although the discrepancy involved in the two methods of measurement is but 1 to 6 mms. of the total path in air, the employment of a difference method magnifies the error to one of 2-fold. Hence, for accurate purposes the microscopic method is preferable. It has the disadvantage that it can only be applied after destruction of the bulb, so that the radiometric method will still be essential for preliminary examination in selecting suitable bulbs. The factor for converting glass into air equivalent, used later in the corrections, is 1 cm. air at 20° and 760 mm. ≈ 0.0056 mm. of glass.

¹⁰ Ref. 4a, p. 397. Ref. 3b, p. 76.

dimensions given in Table I are of secondary importance in later calculating the various corrections involved.

In Table II will be found the experimental results in detail for Expt. 1, and immediately following them a summary of results from Expt. 2, obtained in the same way. The calculations of the velocity constants from the observed changes of pressure involve only the two equations previously given.¹¹

$$\frac{k\mu}{\lambda} = \frac{\log \frac{P_0}{P}}{E_0 (1 - e^{-\lambda t})} \tag{1}$$

and
$$\left(\frac{k\mu}{\lambda}\right)' = \frac{\log \frac{P_1}{P_2}}{E_0 \left(e^{-\lambda l_1} - e^{-\lambda l_2}\right)}$$
 (2)

Equation 1 is the form for calculation from the initial pressure P_0 to any pressure P_t through the entire interval of time. Equation 2 is the form for the usual "point to point" method of calculation to show absence of trend in the constant. $\frac{k\mu}{\lambda}$ and $\left(\frac{k\mu}{\lambda}\right)'$ may be regarded, for present purposes, merely as velocity constants, without regard to the significance of the separate symbols.

Table II

Comparison of Velocities for $2H_2 + O_2 = (2H_2O)$ Under the Influence of Radon Experiment 1

Vol., 23.69 cc. Diam., 3.563 cm. E_0 for A, 0.1101 curie; for B, 0.0733 curie

		الماعا الملك المكير	ay build at center of	reaction spirere	
				Velocity of	constant
	Days Tie	de Hrs.	$P(2H_2 + O_2)$ Mm. Hg	$\frac{k\mu}{\lambda}$	$\left(\frac{k\mu}{\lambda}\right)'$
	2	0	540.3		• •
	0	6.00	515.9	9.50	9.50
	0	15.00	483.9	9.41	9.35
The state of the s	1	11.00	424.6	9.47	9.52
September 1	1	23.75	394.8	9.47	9.45

Av. 9.46

B. After breaking α-ray bulb and allowing radon to mix with H₂ and O₂

0	0	404.8		•••
0	7.92	394.0	6.43	6.43
1	6.00	367.4	6.57	6.62
- 2	6.50	343.8	6.64	6.75
2	18.00	334.5	6.66	6.81
	•			

Av. 6.65

For Expt. 2, carried out in the same way between pressure limits of hydrogen plus oxygen (A) 579.7 to 458.1 mm. in 2 days and 0.5 hour, and (B) 453.5 to 358.4 mm. in 7 days and 11.5 hours, the velocity consts. obtained ¹¹ Ref. 3a, pp. 536, 543. Ref. 3b, pp. 96, 108,

were: A,
$$\frac{k \mu}{\lambda} = 7.05$$
; $\left(\frac{k \mu}{\lambda}\right)' = 7.05$, with $E_1 = 0.1094$ curie. B, $\frac{k \mu}{\lambda} = 4.64$; $\left(\frac{k \mu}{\lambda}\right)' = 4.63$, with $E_0 = 0.0690$ curie.

4. Discussion of Results.—This is the first instance in which the manometric course of a gas reaction produced by radon in an α -ray bulb has been determined. While the manipulation involved is far more difficult than that for mixtures (Method B), it is nevertheless essential to use α -ray bulbs in some cases. It is, therefore, gratifying to know that with suitable manipulation they can be used as a source of α radiation which obeys satisfactorily the theoretical previsions.

A direct comparison of the two velocities, Methods A and B for Expts. 1 and 2, as just reported, shows that radon is more effective when radiating from the center than in the mixture in the proportions: $\frac{9.46}{6.65} = 1.42$ and

 $\frac{7.05}{4.63} = 1.52$, which are direct experimental efficiency factors. According to the statements of Section 1, their reciprocals, 0.704 and 0.657, would represent values 12 for the fraction f of the radius being sought, if the average path equal $f \times r$. Evidently the values cannot be accepted without a number of corrections, which largely remove their disagreement.

In order to avoid complication, a full treatment of all the corrections involved in both methods (A) and (B) is presented in a separate paper. It suffices here to enumerate them. The corrections which apply to the α -ray bulb are (1) for tip and neck, (2) correction to zero diameter, (3) for wall thickness and oblique passage of α particles through it. Those applying to the reaction sphere are (4) dead arm for Method A, (5) average intensity of ionization as dependent on the pressure of the reacting gases, (6) recoil atom effect (absent in Method A). By applying these corrections, as shown in detail in the subsequent paper, a final value for that fraction of the radius which is equivalent to the mean path is obtained. That from Expt. 1 is $0.615\ r$ and from Expt. 2 is $0.609\ r$, which values, within the limits of error may be regarded as identical, $(0.61 \pm 0.01)\ r$. This value has been corrected to the following conditions of ionization: sphere of 2 cm. diameter containing air at 320 mm. and 0°. Theoretically, the value $0.61\ r$ holds accurately only for these conditions, and the drift or

¹² Similar results were obtained in two single experiments by Scheuer [Compt. rend., 159, 423 (1914)] but were not of such a character that they could be used to obtain an accurate value of f. Scheuer stated the differences in velocity in terms of M/N values. This is, of course, an error, arising from his employment of the Duane and Laborde formula for calculating ionization in both cases which is not at all permissible for the α -ray bulb. Evidently, it is the length of path and the resultant ionization which is increased by use of the α -ray bulb; the M/N ratios remain constant.

¹³ Bardwell and Doerner, This Journal, 45, 2593 (1923).

diffusion of active deposit to the wall should depend on the length of path times the density of the gas traversed. That one is not dealing with normal diffusion is evident from the results of Debierne.14. So far as these and previous experimental results show, the proportion of active deposit on the wall is constant through quite a range of pressures and diameters. For example, if drift or diffusion has a determining influence, one would expect in Expt. 2 (when both the diameter and pressure were larger than in Expt. 1) to obtain a larger value of f, yet one slightly smaller was obtained. As far as is known at present the fraction of active deposit on the walls may be maintained practically constant by some other influence than diffusion. We assume, therefore, that the mean linear path traversed by α particles in the sphere is constant over a fairly wide range of pressure. The ionization itself, however, will change with pressure along a given path according to the Geiger ionization curve. We give in Table III. therefore, some interpolated values of average intensity of ionization. These data may be used for any other gas or mixture of gases by reducing to the basis of air by means of the specific ionization.

TABLE IIIa

Average Intensity of Ionization for Radon Mixed with Air in a Bulb of 2 Cm. Diameter at 0°

Pressure in mm. of Hg	100	300	500	700	900
Ion pairs × 104 per cm					

^a The number of ions per centimeter of path is based on the value 2.37×10^5 for the total path in air for Radium C. H. Fonovits-Smereker has recently reported [Sitzb. Akad. Wiss. Wien. II_a, 131, 355-63 (1923)] a value 2.20×10^5 . The values in Table 3 may be converted by multiplying by the factor 2.20/2.37, if desired.

It remains to discuss the probability of the result obtained. By referring to Table IV, it will be seen that the value 0.61 r lies well within

		r	ABLE IV	
Assumed Radon	proportions of RaA %	the wall of RaC %	Resulting av. path of α particles in sphere $r \times$	Conclusion
0	0	0	0.750	Maximum possible
0	0	100	.667	Possible
0	100	100	.583	Minimum possible
100	100	100	(.500)	Impossible
0	84.0	84.0	.61	Found
0	77.2	90.8	.61	Found
pro	ning chemica portional to l t to ionizat	inear path		
	ticles.		(.53)	Impossible

the theoretical limits (0.58 to 0.75 r), which is a further independent confirmation of the average-path theory of α -ray chemical action. An in¹⁴ Debierne, "Le Radium," 6, 97 (1909).

terpretation of the result is possible from the standpoint of distribution. For 90.8% RaC¹⁵ on the wall at the time of α -ray emission, the value 0.61 r will be satisfied by 77.2% of RaA on the wall. This distribution is intermediate between that to be expected if deposition were controlled solely by the rate of reaching the wall (taking into account the decay rates of RaA, and RaC through RaB) and that previously assumed by Lind³ of 100% deposition of both RaA and RaC. The value 0.61 r will be used in all future calculations for gas mixtures in small spheres, unless otherwise stated, and will later be used for correcting some previous calculations.

The last line of Table IV will not be clearly understood without reference to the following paper but, in brief, means that a full consideration of the complete or partial suppression of α particles owing to their oblique passage at different angles through the wall of the α -ray bulb, with regard merely to their subsequent *linear* paths through the gas phase and without reference to ionization at all, leads to a value 0.53 r for the average linear path in mixtures, which is less than 0.58 r, the lowest theoretically possible. Hence, the mere *linear relations* without resort to *ionization*, are incapable of explaining the quantity of chemical combination observed. This is further evidence in support of the ionic-chemical hypothesis.

It is a pleasure to acknowledge the valuable assistance of Professor J. C. Jones of the University of Nevada in making the microscopic measurements of the wall thickness of the α -ray bulbs.

Summary

- 1. By means of a chemical comparison method consisting of the measurement of the velocities of combination of electrolytic hydrogen and oxygen under the influence of radon in equilibrium with RaC, (A) when confined in an α -ray bulb at the center of the reaction sphere, (B) when mixed with the gases, it was found that the mean effective path of the α particle (in mixtures) is $0.61 \pm 0.01 \times$ the radius.
- 2. The direct micrometer measurement of the walls of α -ray bulbs showed them to be about half as thick as indicated by the zinc sulfide screen radiometric method.

RENO, NEVADA

¹⁵ Ref. 3a. Ref. 3b, p. 205.

[Contribution from the Rare and Precious Metals Experiment Station of the Department of the Interior, Bureau of Mines, in Coöperation with the Mackay School of Mines, University of Nevada]

CHEMICAL ACTION PRODUCED BY RADON IV. CHARACTERISTICS OF THE ALPHA-RAY BULB AS A SOURCE OF IONIZATION¹

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The corrections necessary to reduce the experimental efficiency factors reported in the preceding paper to the exact value, $(0.61 \pm 0.01) \ r$, (the mean effective path of α particles in a sphere of radius r) will be considered.

The construction of α -ray bulbs was first developed by Lind and Duane and has been described in detail by Lind.² Although very thin bulbs are desirable, there is a practical limit of thinness, dependent on the diameter of the bulb. Moreover, the α -ray bulb is not a perfect spherical shell; it has a fin. t. (Fig. 1) of relatively thick glass and a capillary con-

it has a tip, t, (Fig. 1) of relatively thick glass and a capillary connection m. Alpha particles striking either the tip or mercury in the neck (at the shoulder of the bulb) are lost. This loss should be made as small as possible, but reduction of the diameter of the neck below 0.4 mm. is not practical, for it would be difficult to maintain a perfect setting of the mercury. The column of mercury in a very small neck has a tendency to separate, throwing a droplet of mercury into the bulb, which it is impossible to



Fig. 1

reunite. The complete corrections necessary to establish the α radiation from such bulbs require rather laborious calculations for each set of dimensions. From the manipulative standpoint, bulbs 1.5 mm. in diameter with wall thickness of 0.0025 mm. are most satisfactory. Hence, we have used bulbs as nearly as possible of this size. Our calculations regarding ionization will be rigidly correct only for such α -ray bulbs.

1. Correction for Tip and Neck.—In a bulb of 1.5 mm. diameter, containing radon, we have assumed that RaA and RaC (in equilibrium) are deposited uniformly upon the wall, and that from any point in the bulb or upon the wall, the emission of α particles is uniform in every direction. Let a and b be the solid angles subtended from the center of the bulb by the tip and neck, respectively. The fraction of the total surface represented by the tip and neck is $(a + b)/4\pi$. The fraction of the surface which is effective in radiating is $1 - [(a + b)/4\pi]$. If $k\mu/\lambda$ is the ve-

¹ Published with the permission of the Director of the Bureau of Mines.

² Lind, Am. Chem. J., 47, 400 (1912). "Chemical Effects of Alpha Particles and Electrons." Chemical Catalog Co., N. Y., 1921, pp. 76-77.

locity constant for an actual α -ray bulb, the velocity constant for a theoretically perfect bulb (without tip or neck) is $\frac{k\mu}{\lambda} \cdot \frac{1}{1-\frac{a+b}{4\pi}}$.

- 2. Correction for the Radius of the α -Ray Bulb.—Let r be the radius of the reaction sphere and R be the radius of the α -ray bulb. The distance traversed by an α particle emerging normally from the α -ray bulb is r-R. For the theoretical case of an α -ray bulb of zero radius, the distance traversed would be r. The velocity constant for a theoretical α -ray bulb (with no tip or neck and zero radius) is $\frac{k\mu}{\lambda} \cdot \frac{1}{1-\frac{a+b}{4\pi}} \cdot \frac{\gamma}{r-R}$.
- 3. Calculation of the Effective Average Intensity of Ionization.—In calculating the ionization produced by any given α particle emerging from the bulb and traversing the gas phase, two factors must be considered: (1) the obliquity of passage through the wall; (2) the change of ionization along the path as expressed by the Geiger curve. Evidently (2) is dependent upon (1). The ionization (Fig. 2) from (o) to (l) is represented approximately by an expression of the type, $y = \frac{K}{(R-x)^{1/2}}$ where y is the intensity of ionization at any point x, and R is the range from (o) to (1). The constant K is dependent upon the gas traversed and its pressure. The end of the curve (1) to (m) is nearly a straight line and must be represented by a separate equation. Bragg⁶ showed that the shape of the ionization curve is only approximately the same for all gases when the abscissas are adjusted to represent the same stopping power. Thus, Henderson's curve⁷ for air is not exactly similar to the one found by Geiger for hydrogen. For the electrolytic mixture of hydrogen and oxygen used, we therefore construct a composite curve (Fig. 2) from the separate curves for hydrogen (Geiger) and air (Henderson), giving the hydrogen values double weight. The abscissas are retained as those of air at 20° and 760 mm. pressure. The ranges of α particles from Rn, RaA and RaC are taken as 4.23, 4.83 and 7.06 cm., respectively. For the pressure changes in Expts. 1 and 2 of the preceding paper the path of an α particle from the inner to the outer bulb is equivalent to an abscissa difference varying between 0.40 and 0.75 cm. A preliminary set of calculations of the ionization showed that the average intensity of ionization from an α -ray bulb

³ The correction for oblique rays is taken up in Section 3.

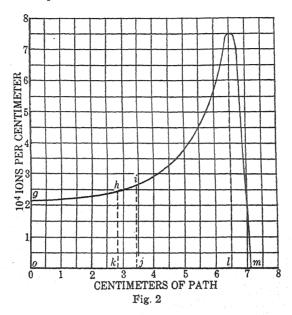
⁴ The effect of obliquity was treated graphically by Lind in ozone formation (Ref. 2). In those experiments, the reaction chamber was so large that no α particles reached the outer wall, so that Correction 2 did not arise.

⁵ Geiger, Proc. Roy. Soc., 83A, 505 (1910).

⁶ W. H. Bragg, "Studies in Radioactivity," 1912, Chapters 5 and 6.

⁷ Henderson, Phil. Mag., 42, 538 (1921).

is constant through this range of path. We therefore calculate the effective average intensity of ionization of α particles emerging from an α -ray bulb as used in these experiments as follows.



Consider a point b on the inner surface of the α -ray bulb shell abc (Fig. 3). θ is the angle between the oblique pencil of rays bc and the

normal pencil bd. For increasing values of θ , the path through the glass wall increases until at 87° no α particles, even from RaC, emerge from the bulbs used. For angles of θ greater than 90°, the pencil passes through the interior of the α -ray bulb before it reaches the wall. However, the wall thickness traversed by such pencils is the same as for the supplementary angle, due to the symmetry of a secant intercepting the walls

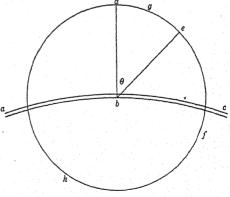
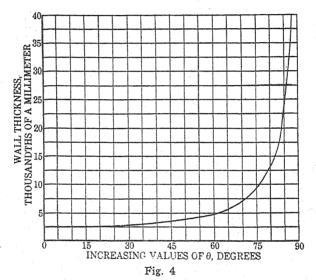


Fig. 3

of a spherical shell. It is therefore necessary to consider only the average effect of α particles emerging at angles less than 90°. The thickness of glass traversed for increasing values of θ was calculated geometrically from the diameter and wall thickness. A plot was made of the thickness

as a function of Θ (Fig. 4). The lengths of path (in terms of air) cut off by the shell were listed for the following angles: 0° ; 7.5; 15; 22.5; 30.0, 37.5, 45; 52.5; 60; 67.5; 71.25; 75; 76.8; 78.8; 80.63; 82.5; 84.38; 86.25; 87.2, 88.13, 90.0. They are represented (Fig. 2) by the variable ok. The path in the reaction vessel for each pencil is represented by kj; and the number of ions by the area hijk. The area divided by kj gives an average ordinate for each pencil which we shall call intensity of ionization.

The next step is to determine the relative number of α particles emerging in each pencil. For convenience, circumscribe a sphere of radius bd about the point b (Fig. 3). A circular section dgefh is cut out by a plane through the normal to the surface of the α -ray shell at b. Assume



that the intensity of ionization for a pencil with angle θ_n is the average for the bundle bounded by $\theta_n - \frac{1}{2}(\theta_n - \theta_{n-1})$ on one side and by $\theta_n + \frac{1}{2}(\theta_{n+1} - \theta_n)$ on the other, where θ_n is the *n*th angle. The bundle thus bounded we designate as $\Delta\theta_n$. Further reduction (see list given above) of the size of $\Delta\theta_n$ does not appreciably increase the accuracy of the summation that follows. If $\Delta\theta_n$ is revolved about the normal bd, it cuts out a zone of revolution from the circumscribing sphere. The area of this zone divided by half the area of the circumscribing sphere represents the fraction of α particles emerging in the bundle $\Delta\theta_n$.

An additional variable must be considered. In Section 2 a correction for the radius of the α -ray bulb was discussed. The distance traversed by an α particle from the inner to the outer bulb is also a variable and a function of Θ . As Θ increases, this distance increases. To correct for this increase in distance, the fraction of α particles in the bundle $\Delta\Theta_n$ is

weighted by multiplying by the ratio of the distance at the angle θ_n to the normal distance.

A summation of the products of the intensity of ionization for each bundle by the effective fraction of α particles emerging in the bundle, gives the effective average intensity of ionization of all the α particles emitted by one of the radioactive elements. These calculations were made for RaA and RaC (assumed to be on the wall of the α -ray bulb) and for Rn (gaseous distribution). For radon (gaseous distribution) the α -ray bulb was divided into eight spherical shells. The average intensity of ionization was calculated for the mean radius of each shell and multiplied by the percentage of the volume included. Since the average intensity of ionization increases more rapidly for points near the surface, outer shells were chosen to contain smaller volumes. The average for the three sets will be designated as I_A . For Expt. 1A (preceding article), $I_A = 2.659 \times 10^4 \frac{\rm ions}{\rm cm}$ (referred to

air at 20°, 760 mm.) and for Expt. 2A, $I_A = 2.645 \times 10^4 \frac{\text{ions}}{\text{cm}}$

4. Correction for Dead Arm.—As explained in the preceding paper, a dead arm containing gas which is not radiated was necessitated in mounting α -ray bulbs for Expts. 1 and 2. The quantitative effect of the dead arm upon the velocity constant is easily deduced by examining the differential equation for the rate of change in pressure. Let $-\frac{dP}{dt} = k \mu E_0 e^{-\lambda t} P$ for the case where there is no dead arm. If a dead arm is attached the effectiveness of the α particle is not altered, and hence the same number of molecules react per unit time. But the total volume of gas has been increased by the volume of the dead arm; therefore the rate of change in pressure with dead arm will be equal to $\frac{\text{vol. of bulb proper}}{\text{vol. of bulb proper} + \text{dead arm}}$ rate of change of pressure without dead arm. These relations are not altered in the integrated form of the velocity equation. The velocity constant in Expts. 1A and 2A would be, if there were no dead arm, equal to: $\frac{k\mu}{\lambda}$ (Expt.1) $\times \frac{\text{vol. of bulb proper} + \text{dead arm}}{\text{vol. of bulb proper}}$. The numerical substitution of values for these corrections in Expts. 1 and 2 will be deferred until the corrections for mixtures are discussed.

- 5. Average Intensity of Ionization when Radon is Mixed with the Gases.—A method similar to that employed in Section 3 was used to calculate the average intensity of ionization in mixtures. The method of obtaining average ordinates was different in that, for the case of mixtures,
- 8 A few oblique α particles are probably directed into the dead arm, but they are at least compensated by those oblique α particles which are lost in the projections of the tip and neck of the α -ray bulb outside the bulb.

no part of the path of an α particle is cut off by glass before it traverses the gas phase. The method of weighting was identical with that in Section 3. Values of θ from 0° to 180° in intervals of 7.5° , were used. Calculations were made, first, for RaA and RaC assumed to be on the wall of the reaction sphere; second, for gaseous distribution of Rn, RaA and RaC. To obtain the values for gaseous distribution, the average intensity of ionization was calculated for five points along the radius of the reaction sphere so placed as to be the average radius for approximately equal volumes of gas. For radon the average intensity of ionization for points on the wall and at the center were, respectively, 2.518×10^4 and 2.576×10^4 ions per cm. The values for the other points lay at approximately equal intervals between these two values. We therefore took the mean of the two extremes. For Radium A, the average intensity of ionization is less than 1% higher for gaseous distribution than for the wall, and for RaC it is the same in both cases. It is therefore unnecessary to make any assumption in regard to the distribution of RaA and RaC. The average intensity of ionization for the three sets of α particles, in mixtures we designate as I_B . For Expt. 1B (at 350 mm.), $I_B = 2.375 \times 10^4 \frac{\text{ions}}{\text{cm}}$ (referred to air at 20° and 760 mm.); and for Expt. 2B (at 450 mm.), $I_B = 2.398 \times 10^4 \frac{\text{ions}}{\text{cm}}$.

6. Recoil Atom Effect.—Lind⁹ has shown that recoil atoms from Rn, RaA and RaC produce chemical action to an extent which cannot be neglected in Expts. 1B and 2B. 10

The combined chemical effect of α rays and recoil atoms is double the α -ray effect at 116.8 mm. of electrolytic hydrogen and oxygen in a sphere of 1 cm. diameter. Assuming that the relations are similar in large bulbs (for example that in one of 2 cm. diameter the rate is doubled at a pressure of 116.8/2 mm., etc.) the relative effects can be calculated for the mixtures in Expts. 1 and 2. Evidently recoil atoms are absent when α -ray bulbs are used, which also has recently been experimentally proved. ¹⁰

In Expt. 1B at a pressure of 350 mm. the α -ray effect is 91.6% of the combined effects. In Expt. 2B, at a pressure of 450 mm. it is 94.4%.

7. Application of Corrections.—The velocity constants for Method A, referred to a perfect α -ray bulb of zero radius, no dead arm, and to the initial ordinates of the ionization curve for all three sets of α -particles are:

Expt. 1A,
$$9.46 \times 1.0626 \times 1.0466 \times \frac{2.330}{2.659} \times 1.0488 = 9.67$$
; Expt. 2A,

⁹ Lind, This Journal, 41, 533 (1919).

¹⁰ The reality of the recoil atom effect has been verified by new experiments which will be described subsequently. The new data are used for the corrections, but do not differ greatly from the previous results.

$$7.05 \times 1.0564 \times 1.0353 \times \frac{2.330}{2.645} \times 1.02647 = 6.97.$$

The velocity constants for pure α -ray effect corrected for volume of "magnetic capsule," and referred to initial ordinates on the ionization curve are: Expt. 1B, $6.65 \times 0.995 \times 0.916 \times \frac{2.33}{2.375} = 5.95$; Expt. 2B, $4.64 \times 0.996 \times 0.944 \times \frac{2.33}{2.398} = 4.24$.

The average path in Method A is the radius of the reaction sphere. Therefore, the average path in Method B is for Expt. 1 equal to $\frac{5.95}{9.67} \times r =$

0.615 r, and for Expt. 2 equal to $\frac{4.24}{6.97} \times r = 0.600$ r. These values are reported and discussed in the preceding paper.

It was found from the data obtained by methods described in Section 3, that 94.4% of the α rays get through the α -ray bulb. Assuming that the velocity of reaction is proportional merely to the linear path of the α ray in the gas phase, the velocity constants for Method A (no ionization considerations) are: Expt. 1A, $9.46 \times 1.030 \times 1.0488 \times 1.0626 \times 1.059 = 11.50$; Expt. 2A, $7.05 \times 1.024 \times 1.02647 \times 1.0564 \times 1.059 = 8.28$. The velocity constants for Method B are: Expt. 1B, $6.65 \times 0.995 \times 0.916 = 6.06$; Expt. 2B, $4.64 \times 0.996 \times 0.944 = 4.36$.

The average path in mixtures would be for Expt.1 equal to $\frac{6.06}{11.50}r = 0.527r$, and for Expt. 2 equal to $\frac{4.36}{8.28}r = 0.527r$, or to the limits of accuracy, 0.53 r. This value has no reasonable interpretation and is discussed in the preceding paper.

Summary

For the corrections involved in Part III, a knowledge of the characteristics of the α -ray bulb as a radiator, as affected by the tip and neck, by the thickness of the wall and obliquity of passage of α particles through it, and by the diameter of the bulb (reducing it to zero dimensions in order to afford radiation from a point source) is necessary. In addition, the other corrections applying to the outer sphere itself are treated, such as the deadarm correction and the change of ionization intensity with the pressure. The recoil atom effect is also used as a correction for the results, to reduce them to the same conditions as those obtaining outside the α -ray bulb, through which recoil atoms cannot penetrate.

RENO, NEVADA

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE INTERFERENCE OF COBALT IN THE BISMUTHATE METHOD FOR MANGANESE!

By G. E. F. LUNDELL²

RECEIVED AUGUST 9, 1923

The conditions recommended by Blum³ for the determination of manganese by the bismuthate method are as follows: "To the manganese solution containing 20 to 40% (by volume) of nitric acid (free from nitrous acid) in a volume of 50 to 150 cc., add a slight excess of bismuthate (usually 0.5 to 1.0 g.), agitate thoroughly for about one-half minute, wash down the sides of the flask with 3% nitric acid, filter through asbestos, wash with 100 cc. of 3% nitric acid, add a slight excess of ferrous sulfate, and titrate at once with permanganate."

To these may be added the following: (1) the solution should not contain more than 0.05 g. of manganese; (2) moderate amounts of sulfuric acid are not harmful, as for instance 5 cc. of sulfuric acid and 10 cc. of nitric acid in a 50 cc. solution; (3) chlorides must be absent; (4) the temperature of the solution may be varied from 5° to 25°; (5) one-half minute is enough for the reaction if the solution is agitated, but a longer period will do no harm; (6) new, and also stored, bismuthate should be tested for its oxidizing power; this is easily done by trying the bismuthate method on portions of permanganate solution which have been reduced and comparing the consumption of ferrous sulfate with that obtained by direct titration; (7) unless the asbestos has been very carefully freed from hydrochloric acid and chlorides, the first run through it will always be low; to make certain, it is well to pass through the filter a dil. nitric acid solution of permanganate containing a small amount of bismuthate and then to wash it with 3\% nitric acid before regular filtration; (8) the ferrous sulfate solution should not be allowed to stand for more than 10 minutes before the titration with permanganate, and its permanganate equivalent is best found by the titration of a suitable volume of ferrous sulfate which has been added to the filtrate obtained in a blank run on the bismuthate, acid, filtration, etc.; (9) the permanganate solution which may be either 0.03 or 0.1 N depending on the percentage of manganese involved is best standardized against sodium oxalate as described by McBride,4 and a properly prepared and filtered solution should preserve its strength for several

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³ Reprint 186 of the *Bulletin* of the Bureau of Standards, 8, 736 (1912). This Journal, 34, 1395 (1912).

⁴ McBride, *ibid.*, **34**, 415 (1912).

months exposed to diffused light, if protected from dust and reducing substances. In the presence of the latter, solutions containing potassium hydroxide decompose less rapidly than do neutral solutions.³

For amounts of manganese up to 0.05 g. the accuracy of the above method can be safely regarded as within 1 part in 500. The procedure is singularly free from interference by other elements, and the only elements that have been recognized as troublesome are chromium and cerium. Some elements introduce minor difficulties as, for example, the color interference of concentrated solutions of copper or nickel salts, the delayed end-point caused by vanadium, the slightly low results caused by antimony, and the slightly high results caused by silver.

Vanadium causes trouble because it is at first oxidized to the quinquevalent state, then reduced to the quadrivalent condition, and finally reoxidized with some difficulty by the very small excess of permanganate which is permissible at the end-point. If it is not completely reoxidized, the results for manganese will of course be high.

Antimony is also oxidized to the quinquevalent state by sodium bismuthate, but only a very small part is reduced by ferrous sulfate in the cool solution which is employed. In further contrast to vanadium, antimony causes the results to be slightly low as, for example, 0.0109 instead of 0.0111 g. of manganese in the presence of 0.05 g. of antimony. Neither the cause of the error nor any remedy save prior removal of the antimony or the use of another method is known to me. If another method is used, Ford's⁵ is to be preferred for accurate analyses, and the persulfate-arsenite method for routine analyses.

Silver introduces slight difficulties as it causes the formation of oxides of nitrogen. The effect is not serious with ordinary amounts of silver as shown by the results 0.0112 and 0.0113 instead of 0.0111 g. of manganese in the presence of 0.01 and 0.1 g., respectively, of silver.

Chromium interferes because it is never completely oxidized at any stage. Only a part of it is oxidized by bismuthate and permanganic acid at the start; this is then reduced by ferrous sulfate, and finally a much smaller part is reoxidized during the final titration. Chromium therefore tends to cause results for manganese to be high. As either oxidation proceeds slowly in cool solutions, good results for manganese can be obtained in the routine analysis of steels containing moderate amounts of chromium and no vanadium by working rapidly (½ to 1 minute reaction) with solutions at a temperature not over 20°. Under such conditions, and especially if ice-cold solutions are used, vanadium causes some trouble as it is reoxidized with difficulty. Hence, such a method works quite well with chrome-nickel, but not so well with chrome-vanadium steels.

⁵ Blair, "The Chemical Analysis of Iron," 8th ed., J. B. Lippincott and Co., 1918, pp. 108-110.

Satisfactory results can be achieved with both steels by using suitable reducing solutions in place of ferrous sulfate, as for example sodium arsenite or mercurous nitrate, which reduce permanganate but not chromate or vanadate.

Cerium is rapidly oxidized to the quadrivalent state by bismuthate (even in cold solution) and subsequently reduced by ferrous sulfate to the trivalent state. Hence cerium will cause high results for manganese unless it is previously removed or a proper reducing agent, such as sodium arsenite, substituted for ferrous sulfate.

Cobalt, in contrast with all of the above, is a real interfering element in the bismuthate method and must be removed if bismuthate is to be used.⁷ This follows because it is oxidized by bismuthate at all temperatures that are permissible for manganese, and the oxidized compound reacts with both ferrous sulfate and permanganic acid. Cobalt upon oxidation approaches the formula Co₃O₄ and the color changes from pink to green.⁸ The oxidized compound reacts with ferrous sulfate, but not directly with permanganic acid. If, however, it is first treated with manganous nitrate and then with permanganate, a reaction does take place as evidenced by a change of color to an amber tint. This solution in the course of time shows a reappearance of the permanganate tint and yields a brown deposit of manganese dioxide together with some oxide of bismuth. The reaction between the oxidized cobalt compound and permanganic acid waits, therefore, upon some decomposition of the latter. When once started, it proceeds with considerable rapidity, and as the resultant compound does not react rapidly with ferrous sulfate, the net result is a lowered consumption of ferrous sulfate with consequent low values for manganese. The extent of the effect is indicated in Table I. In every case measured portions of a standard permanganate solution were reduced by sulfur dioxide, boiled to expel gas, cobalt was added as shown and then enough nitric acid to obtain 40 cc. of a 30% (by volume) solution. This solution was then cooled to 15-20°, treated with an excess of bismuthate, shaken occasionally during three minutes and then diluted with 50 cc. of 3% (by volume) nitric acid, filtered through asbestos and washed with the same acid. The solution was finally treated with a measured excess of ferrous sulfate and titrated with standard permanganate.

- ⁶ F. J. Metzger, This Journal, 31, 523 (1909).
- ⁷ So far as I know, no reference to its behavior in the bismuthate method has been made, save the note "This method (the bismuthate) cannot be used in the presence of cobalt" recommended by me and inserted in the Tentative Methods for the Analysis of Plain Carbon Steel, *Proc. Am. Soc. Testing Materials*, 22, Part I, p. 589 (1922).
- ⁸ A similar and striking change also takes place when a dil. sulfuric acid solution of cobalt sulfate is electrolyzed in a U-tube with moderately long limbs. The liquid in the cathode limb remains pink while that in the anode gradually turns green. Low current must be used, as the oxidized compound is unstable in a warm solution.

TABLE I

The Effect of Cobalt in the Bismuthate Method for Manganese Weight of manganese added, 0.0110 g.

Co added, g	none	none	0.001	0.005	0.010	0.020
Mn indicated, g			0.0107	0.0103	0.0101	0.0094
Error, mg	0.0	0.0	-0.3	-0.7	-0.9	-1.6

Somewhat better, though still unacceptable, results are obtained as shown in Table II, when the oxidized solution is titrated with sodium arsenite

TABLE II

THE EFFECT OF COBALT IN THE BISMUTHATE-ARSENITE METHOD FOR MANGANESE Weight of manganese added, 0.0110 g.

Co added, g	none	none	0.001	0.005	0.010	0.020
Mn indicated, g	0.0110	0.0110	0.0107	0.0106	0.0102	0.0102
Error, mg	0.0	0.0	-0.3	-0.4	-0.8	-0.8

It may be mentioned in passing that cobalt is not oxidized by persulfate in the hot acid solution which is employed for the oxidation of manganese and that, therefore, good results can be obtained in its presence through the use of the persulfate-arsenite method. For standardization work Ford's method⁹ is to be preferred.

In conclusion, I hope that some reader may be stimulated to investigate various methods for the oxidation of cobalt in acid solution. If the oxidation can be carried to a definite stage we shall, of course, have an excellent method for the volumetric determination of cobalt in the presence of such elements as iron and nickel.

Summary

The proper conditions for the determination of manganese by the bismuthate method are reviewed and the interference of certain elements, notably cobalt, is discussed.

Cobalt is oxidized by bismuthate and the oxidized compound reacts with both ferrous sulfate and permanganate. The latter reaction does not start until some permanganate has been decomposed and then proceeds so rapidly that it causes low results for manganese.

In the presence of cobalt, Ford's method is to be preferred for accurate analyses and the persulfate-arsenite method for routine work.

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⁹ Ref. 5, pp. 108 and 110.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

AZIDO-DITHIOCARBONIC ACID. I. FORMATION, PREPARATION AND PROPERTIES¹

By G. B. L. Smith and F. Wilcoxon with A. W. Browne With Microscopical Studies by C. W. Mason Received August 9, 1923

In view of the readiness with which carbon disulfide reacts with salts of hydronitric acid to form the azido-dithiocarbonates,² it was thought possible that it might react directly with free hydronitric acid to form azido-dithiocarbonic acid, as expressed by the equation

$$HN_3 + CS_2 = HSCSN_3 \tag{1}$$

Formation.—Aqueous solutions of hydronitric acid, when shaken with carbon disulfide for several minutes, or when allowed to remain in contact with this substance for several hours at room temperature, yield solutions in which the presence of azido-dithiocarbonic acid may be demonstrated by treatment (1) with a solution of silver nitrate, which precipitates the explosive silver azido-dithiocarbonate, distinguishable from silver trinitride by reason of its insolubility in ammonium hydroxide; (2) with solutions of iodine and hydronitric acid, the reaction between which is strongly catalyzed, as by a solution known to contain azido-dithiocarbonic acid, and (3) with a solution of mercuric chloride, which yields a white precipitate of the explosive mercuric azido-dithiocarbonate. Anhydrous liquid hydrogen trinitride³ reacts with carbon disulfide to form a light yellow product which in its explosive character and in its mode of decomposition closely resembles azido-dithiocarbonic acid.

From sufficiently concentrated aqueous solutions of an azido-dithiocarbonate, mineral acids precipitate the free azido-dithiocarbonic acid. Dilute nitric or sulfuric acid (1:6) acts in this way, but concd. nitric acid oxidizes the azido-acid first liberated, forming some azido-carbondisulfide as an intermediate product, and finally oxidizing at least a part of the sulfur to sulfuric acid.

- ¹ The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article No. 1 under Heckscher Grant No. 60. Parts of this paper were presented at the Svedberg Physical Chemistry Symposium held under the auspices of the Rochester Section of the American Chemical Society, January 19–20, 1923, and at the New Haven meeting of the Society in April, 1923.
- ² (a) Sommer, Ber., 48, 1833 (1915). (b) Browne and Hoel, This Journal, 44, 2106, 2315 (1922). (c) Currier with Browne, ibid., 44, 2849 (1922). (d) See also Oliveri-Mandalà, Gazz. chim. ital., 52, II, 139 (1922). This paper was not seen by the authors until after the manuscript of the present article had been submitted for publication.
- ³ The experiments with anhydrous hydrogen trinitride were performed in this Laboratory by Dr. A. E. McKinney and Mr. R. C. Houck, to whom the authors take this occasion to express their appreciation.

Preparation.—A convenient and satisfactory method for the preparation of azido-dithiocarbonic acid involves treatment of 6 g. of recrystallized sodium trinitride, dissolved in a small amount of water, with 6 cc. of purified⁴ carbon disulfide. The mixture is allowed to react in a small, tightly-corked bottle at 40° for about 48 hours. The resulting solution of the azido-salt is filtered, chilled with ice, and treated with cold concd. hydrochloric acid,⁵ which precipitates the azido-acid. The white, crystalline precipitate is washed three or four times by decantation with ice water, is drained on a Büchner funnel and is finally dried on a porous plate. It is preserved over phosphoric anhydride in a desiccator protected from the light, and kept at a temperature below 10°.

Analysis.—The sulfur was determined by oxidizing weighed samples of the azidoacid, first in alkaline solution with bromine, and then with fuming nitric acid and potassium chlorate, finally weighing the sulfur in the form of barium sulfate.

Analyses. Subs., 0.1851, 0.1903: BaSO₄, 0.7278, 0.7422. Calc. for $HSCSN_3$: S, 53.80. Found: 54.00, 53.56.

The nitrogen was determined in accordance with the usual Dumas method by combustion with copper oxide in a stream of pure carbon dioxide. The sample of the acid was mixed with about 20 g. of fine copper oxide and was heated gradually.

Analyses. Subs., 0.1019, 0.1186: N₂, 27.91 cc. (0.03519 g.), 33.08 cc. (0.04170 g.). Calc. for HSCSN₃: N, 35.26. Found: 35.12, 35.16.

The hydrogen was determined by titration of solutions containing weighed amounts of the solid acid with standard sodium hydroxide solution using methyl orange as indicator.

Analyses. Subs., 0.2587, 0.1087: H, 0.00221, 0.00091. Calc. for HSCSN₃: H, 0.846. Found: 0.856, 0.835.

Further evidence confirming the formula assigned to azido-dithiocarbonic acid was obtained by analysis of the silver salt, prepared by treatment of aqueous solutions of the acid with a slight excess of silver nitrate. This white, insoluble substance is highly explosive in the dry state, but may be handled with comparative safety in aqueous suspension. The precipitate was filtered on a tared Gooch crucible, and was dried at room temperature over phosphoric anhydride for 10 days. In weighing the dry salt, suitable precautions were taken to protect the operator from possible injury. The silver azido-dithiocarbonate was dissolved in fuming nitric acid, the resulting solution was evaporated nearly to dryness, and the silver was precipitated and weighed as silver chloride by the usual procedure.

Analyses. Subs., 0.3765, 0.3767: AgCl, 0.2379, 0.2380. Calc. for AgSCSN₂: Ag, 47.73. Found: 47.56, 47.51.

The foregoing analytical results, considered in connection with the data obtained in a study of the decomposition of azido-dithiocarbonic acid, strongly confirm the structural formula assigned to this compound, H—S—C(=S)—N=N=N.

⁴ Ref. 2c, p. 2851.

⁵ Sommer (Ref. 2a, p. 1841) obtained a white precipitate, which he surmised to be free azido-dithiocarbonic acid, by treatment of a cold, concentrated solution of sodium azido-dithiocarbonate with concd. hydrochloric acid. No evidence was submitted in support of this belief, however, and no further work in this direction was reported.

Properties.—Azido-dithiocarbonic acid is a white or very light yellow crystalline solid. It is fairly soluble in water, and is much more soluble in ethyl alcohol, methyl alcohol, diethyl ether, benzene, carbon disulfide, and glacial acetic acid. If the SCSN₃ group be considered as a unit, azido-dithiocarbonic acid may be regarded as a halogenoid hydracid that bears the same relation to azido-carbondisulfide⁶ that hydrochloric acid bears to free chlorine. It may be titrated with a standard alkali solution using methyl orange or methyl red as indicator. By electrometric titration⁶ it has been found to be nearly as strong an acid as hydrochloric acid. Determinations of the molecular weight of the acid in aqueous solution by the cryoscopic method gave results ranging from 72 to 87, which indicate that the compound is highly dissociated, doubtless in accordance with the expression

$$HSCSN_3 \rightleftharpoons H^+ + SCSN_3^-$$
 (2)

Aqueous solutions of azido-dithiocarbonic acid react with various oxidizing agents including, for example, iodine in potassium iodide solution, nitric acid of suitable concentration, ferric chloride, potassium persulfate, hydrogen peroxide, manganese dioxide, and potassium permanganate, with formation of azido-carbondisulfide which appears as a white, microcrystalline precipitate. This formation of the free halogenoid by oxidation of the halogenoid hydracid takes place as expressed by the equation

$$2HSCSN_3 + O = (SCSN_3)_2 + H_2O$$
 (3)

and corresponds with the liberation of chlorine by oxidation of hydrochloric acid.

Azido-carbondisulfide is itself oxidized by the stronger oxidizing agents, and this substance is, therefore, formed only as an intermediate product when the acid is treated with an excess of such substances as concd. nitric acid or potassium permanganate. In these cases the chief final products of oxidation are sulfuric acid, carbon dioxide and nitrogen.

Solutions of such salts of the heavy metals as silver nitrate, mercuric chloride, lead nitrate and copper nitrate, when treated with a solution of the azido-acid yield the insoluble azido-dithiocarbonates, all of which are highly explosive in the dry state. The acid has only a very slight solvent action upon freshly precipitated ferric hydroxide.

Microscopic Examination.—Crystals of azido-dithiocarbonic acid formed on the microscope slide (1) by interaction of a coned. aqueous solution of the potassium salt and coned. hydrochloric acid, and (2) by re-

⁶ See Browne, Hoel, Smith and Swezey, This Journal, 45, 2541 (1923).

⁷ The experimental work on this topic has been carried out by Mr. George H. Brandes, Instructor in Analytical Chemistry at Cornell University. The data will be published in the near future, in connection with an investigation of the electrical conductance of azido-dithiocarbonic acid and certain of its salts, now nearing completion in this Laboratory.

crystallization of samples of the acid previously prepared on a large scale, were found to be identical in appearance.

The simplest setting would place them in the monoclinic system with the forms clino pinacoid (010), basal pinacoid (001) and unit prism (110) represented. The angle β is about 56°. The angle between the prism faces in the basal plane is about 83°. Twinning is frequent on the basal plane.

Double refraction is strong; the extinction angle (clino-pinacoidal view) is about 30°, and the basal view shows parallel extinction. The index of refraction for vibrations 30° to c is estimated at 1.6; for vibrations transverse to this, 1.35+. Such interference figures as were obtainable indicate biaxial character, 2 E large. Z is apparently the acute bisectrix, making the crystals optically positive (+). Probable orientation: $X \land c = 30^\circ$; $Y \perp a$; Z = b.

Contact with a hot wire (below red heat) causes the acid to detonate with a puff of smoke and sulfurous odor, but the detonation is much less violent than that of azido-carbondisulfide. The residue consists of a pale yellow oil from which gas is evolved in considerable amount. Minute prismatic, strongly birefringent crystals, probably of azido-carbondisulfide, showing parallel extinction are a product of the detonation, and are found in colorless masses, vesicular because of the oily material in the interstices. These crystals disappear on standing in contact with the oily material, with evolution of gas, and formation of more oily material. This oil gradually darkens in color and increases in viscosity, with ultimate formation of a red-orange, vesicular, brittle substance, very similar in appearance to the end-product of the decomposition of azido-carbondisulfide.

At room temperature the solid azido-dithiocarbonic acid decomposes slowly, with evolution of gas and formation of a small amount of a fine-grained anisotropic crystalline material together with the yellow oil. Within 24 hours the whole sample is transformed into a yellow, vesicular, tenacious "dough" of viscous material, which after 2 or 3 days becomes brittle and is found to contain no crystalline material.

When brought into immediate, intimate contact with freshly prepared dry azido-dithiocarbonic acid, the yellow detonation product appears to accelerate appreciably the rate of decomposition. This was demonstrated by evaporating a solution of the acid to a crystalline film on a microscope slide. Upon this film was placed a small amount of the coarsely crystalline acid, which was then carefully detonated with the aid of a hot wire. Care was taken to avoid contact between the wire and the microcrystalline film, which as a result of the explosion of the coarse, supernatant material, was spattered with the yellow oil. Wherever this substance came into contact with the undecomposed acid an erosion of the crystals and evolution of gas took place at a rate more rapid than that of the normal, slow decomposition, and quite distinct from the last evolution of gas from the detonation product itself.

The yellow oil obtained as an intermediate product of the decomposition of the azido-acid catalyzes not only the spontaneous decomposition of the acid itself, but also that of the related compound, azido-carbondisulfide. Conversely, the very similar yellow oil obtained from the azido-disulfide catalyzes not only the decomposition of this substance itself but also that of the azido-acid.

Decomposition.—Azido-dithiocarbonic acid is sensitive both to shock and to heat. The dry crystals detonate when broken in a porcelain mortar, when rubbed on a porous plate, or when heated on an asbestos board. The explosion is in no case so violent, however, as that of azido-carbon-disulfide under similar conditions. It is accompanied by the liberation of much heat with considerable smoke and flame, as well as a characteristic odor resembling that of sulfur monochloride.

Below 10° the compound is relatively stable, especially when protected from the light. Even at 0°, however, it undergoes slow decomposition when exposed to the action of daylight. At room temperature, and exposed to diffused daylight, the white or very light yellow azido-dithiocarbonic acid spontaneously passes through a series of color changes which may be formulated as YT1, Y, and OY on the Milton Bradley chart.8 During the course of these changes the dry crystalline material becomes viscous in texture, and puffs up, as a result of the liberation of gas, to several times its original volume. Weighed samples of the acid were found to undergo a loss of weight somewhat in excess of that corresponding to the evolution of 2 atoms of nitrogen per molecule. The presence of appreciable quantities of thiocyanic acid was established by allowing the gaseous products of decomposition to impinge upon filter paper moistened with a solution of ferric chloride. The resulting deep red color was discharged by a solution of mercuric chloride, but not by dil. hydrochloric acid, indicating the presence of thiocyanic acid and the absence of hydronitric acid. Thiocyanic acid vapor accelerates the spontaneous decomposition of azido-dithiocarbonic acid. This was demonstrated by allowing the vapor obtained by treatment of ammonium thiocyanate with dil. sulfuric acid to impinge upon a sample of the azido-acid. It was further shown in unexpected fashion when 5 samples of the solid acid, each of which weighed from 0.5 to 1.0 g., contained in small porcelain crucibles placed close together and covered with one large enamelled iron basin, detonated successively, after shortening time intervals, owing to the increasing concentration of thiocyanic acid in the surrounding atmosphere. The accumulation of the liquid (or solid) products of decomposition in close contact with the still undecomposed portion of the sample also results in greatly decreasing the stability of the azido-acid. Rela-

⁸ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1st ed., 1905, vol. I, p. 232.

tively large samples of the compound and samples piled up or closely packed together are more subject to spontaneous explosion than are smaller portions or thin layers, owing to the greater opportunity for adsorption of the catalytic agent in the former case. Such samples have been observed to explode, in some instances even at the temperatures of the ice chest, after the accumulation of catalyst during several hours of slow, spontaneous decomposition.

Very small samples of the azido-acid, heated in open melting-point tubes, appear to melt between 50° and 65° to a yellow oil, in reality a decomposition product, which undergoes further transformation, with evolution of gas and formation of the final orange-yellow solid product. Many samples have exploded under this treatment, sometimes with sufficient violence to shatter the melting-point tube, and in two instances, the thermometer as well. When heated above 70° samples of the azido-acid have almost invariably exploded, usually within a few seconds.

In aqueous solution azido-dithiocarbonic acid undergoes decomposition, with evolution of nitrogen and formation of the usual orange-yellow product which is insoluble in water. The solution becomes turbid at first probably owing to the formation of small amounts of an insoluble intermediate product, rather than to the formation of sulfur, as the substance was found to be soluble in hydrochloric acid. In certain non-aqueous solvents such as carbon disulfide, benzene, and ethyl alcohol, the azido-acid undergoes a similar decomposition with formation, apparently, of the same final product, which is insoluble also in these liquids.

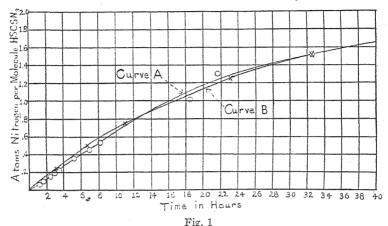
A quantitative nitrometric study of the isothermal decomposition of azido-dithiocarbonic acid in aqueous solution at 25° has been made over a period of about 218 hours, during which the volume of nitrogen evolved was read at frequent intervals. A sample of the solid acid weighing 0.1024 g. and treated in the nitrometer tube with an amount of water just about sufficient to dissolve it, yielded 19.22 cc. (corr.) of nitrogen gas, corresponding to 1.991 atoms of nitrogen per molecule of the azido-acid. The data are shown in part in Fig. 1, Curve A. They indicate that the azido-acid decomposes in aqueous solution at a continually decreasing rate, owing to the diminishing concentration of the reacting substances present in the solution. The differential equation

$$\frac{\mathrm{d}x}{\mathrm{d}T} = 0.04368 (2-x) \tag{4}$$

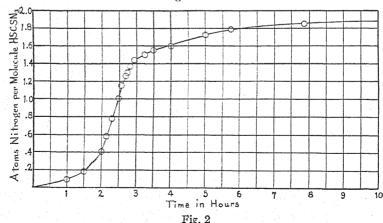
where T is the time in hours, and x the number of atoms of nitrogen evolved per molecule of the azido-acid, expresses the approximate velocity of the reaction. This is the type equation of a simple monomolecular reaction. The integrated form

$$T = \frac{1}{0.04368} \left(\ln \frac{2}{2 - x} \right) \tag{5}$$

makes it possible to calculate the amount of decomposition at any specified time. Curve B, Fig. 1, was plotted from data calculated by means of Equation 5. From the close agreement between the experimental and the calculated data it is evident that the spontaneous decomposition of azido-dithiocarbonic acid in aqueous solution is to be regarded as a simple, monomolecular reaction that shows no effect of catalytic action.



A similar investigation of the isothermal decomposition of the dry azido-acid at $25\,^{\circ}$ covered a period of 48 consecutive hours, during which a sample weighing 0.1055 g. yielded 18.76 cc. (corr.) of nitrogen, or 1.987 atoms per molecule of the acid. The course of the decomposition during the first 10 hours is shown in Fig. 2.



The form of the curve tends strongly to confirm the experimental observations upon the catalytic action of the yellow intermediate product recorded above, and points toward the conclusion that the decomposition

of dry azido-dithiocarbonic acid takes place after the fashion of a monomolecular reaction catalyzed by one of its own products. It has not been found possible to formulate this autocatalytic reaction mathematically by means of the type equation $\mathrm{d}x/\mathrm{d}t = kx(A-x)$, probably for one or more of the following reasons: (1) at least a part of the catalyst is initially evolved as a gas, HSCN, the adsorption and polymerization of which takes place to a degree largely dependent upon the mechanical and physical condition of the sample; (2) the reacting mixture is only partially in liquid form, with the result that its behavior cannot be satisfactorily interpreted in terms of the mass law; and (3) light may exert a catalytic effect upon the reaction as indicated by certain qualitative observations. Further investigation of this topic is in progress.

In the case of the decomposition of the azido-acid in aqueous solution the catalyst is but slightly soluble in water and is, therefore, removed from the sphere of action as soon as it is formed. Very dilute aqueous solutions of the unpolymerized thiocyanic acid seem to exert no appreciable catalytic influence upon the reaction.

It might be argued that at higher temperatures the rapid progress of the exothermic decomposition would maintain the sample of azido-acid at a temperature appreciably above that of the thermostatic bath, thus producing an apparent autocatalytic effect due to the action of heat. At ordinary temperatures, however, the thermal gradient established in this manner may be regarded as negligible, in view of the relatively long period of decomposition, especially in cases where small samples of the azidoacid are used.

Various lines of evidence justify the conclusion that azido-dithiocarbonic acid, both in the dry state and in aqueous solution, decomposes as expressed by the equation

$$HSCSN_3 = HSCN + S + N_2$$
 (6)

This is in conformity with the results of independent investigations of the decomposition of the potassium azido-salt, which yields potassium thiocyanate, sulfur and nitrogen; and of azido-carbondisulfide, from which are obtained free thiocyanogen, sulfur and nitrogen.

The brittle, vesicular, orange-yellow, final product was found¹¹ to be somewhat soluble in hot water, but practically insoluble in cold water. It dissolves readily in solutions of potassium, sodium or ammonium hydroxide. It loses little or no weight when stored for days in a desiccator over phosphorus pentoxide. It is apparently but slightly soluble in ethyl alcohol, acetic acid, and acetone.

⁹ Ref. 2b, p. 2318.

¹⁰ Ref. 6, p. 2543.

¹¹ In connection with this work the authors acknowledge with pleasure the assistance rendered by Mr. D. P Murray.

Four determinations of the total amount of sulfur in both free and combined forms showed an average of 70.18%, confirming the theoretical value, 70.35%, calculated for the mixture (HSCN)_x + xS. The sulfur appears to be very intimately and rather uniformly mixed with the polymerized thiocyanic acid, possibly forming a molecular mixture or solid solution with it. In an attempt to extract the sulfur with carbon disulfide it was found that the extract contained some thiocyanic acid, showing a tendency on the part of this liquid to dissolve or depolymerize the residue. A fair separation was accomplished by digestion of the mixture with a 5% solution of sodium hydroxide. This dissolved the polymerized acid, and left much, though probably not all, of the sulfur undissolved. After removal of the sulfur by filtration, the yellow filtrate was acidified with nitric acid in slight excess, with the result that a heavy orange-yellow precipitate, similar in appearance to the original mixture, was obtained. The percentage of sulfur in different samples of this product was found to vary between 53 and 55%, but the average of several determinations, 54.21%, agrees closely with the theoretical value, 54.26%calculated for thiocyanic acid, indicating that the product is a fairly pure polymerized thiocyanic acid. It probably resembles the substance already described as dithiocyanic acid, H₂C₂N₂S₂;¹² while the orange-yellow solid regarded by the authors as a mixture of free sulfur and polymerized thiocyanic acid shows certain of the characteristics of the substance known as perthiocyanic acid, H₂N₂C₂S₃, 13 or as isopersulfocyanic acid, H₂C₂N₂S₃. 14

Summary

Azido-dithiocarbonic acid, HSCSN₃, a new halogenoid hydracid, has been prepared by treatment of concentrated solutions of the sodium salt with hydrochloric acid. Its composition has been established by analysis, and its crystallographic and optical properties have been studied under the microscope. It is a white or very light yellow crystalline solid, fairly soluble in water, and readily soluble in various non-aqueous liquids. It shows the characteristic properties of a strong acid, and its strength approaches that of hydrochloric acid. It is easily oxidized by various reagents, yielding the free halogenoid, (SCSN₃)₂.

In solid form the acid is sensitive both to shock and to heat. At ordinary temperatures it undergoes spontaneous decomposition at a rate characteristic of reactions of the monomolecular type. This decomposition is catalyzed in the dry state, but not in aqueous solution, by an intermediate product or by the thiocyanic acid formed, and may be expressed

¹² Fleischer, Ann., 179, 204 (1875).

¹³ Chattaway and Stevens, J. Chem. Soc., 71, 833 (1897). See also Klason, J. prakt. Chem., [2] 33, 116 (1886); 38, 366 (1888).

¹⁴ Stokes, This Journal, 29, 443 (1907).

by the equation, $HSCSN_3 = HSCN + S + N_2$. The solid product finally formed consists of polymerized thiocyanic acid and free sulfur.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

DENSITY AND HYDRATION IN GELATIN SOLS1

By The Svedberg and Bruno A. Stein

RECEIVED AUGUST 11, 1923

Introductory and Theoretical

It is known that in the case of true solution and in colloidal solutions there is more or less combination between the solute or the particles and the solvent or dispersing phase.

Nägeli long ago advanced the idea that solution was a process in which the material was surrounded by a shell of water. Pauli² states, "Crystalloids are said to be hydrated (or, in general, solvated) in solution when water is attached to the dissolved molecules in a stoichiometric proportion. In some instances this hydration is sharply defined (as for sulfuric acid and ferric chloride), but in other cases the hydration is variable and shows a continual alteration with dilution and with change of temperature. We can describe such phenomena with more accuracy as addition of water (or formation of envelopes) by the particles,"

"Such an addition of the medium occurs on the particles of many colloids, and is described as hydration. . . . The indications of hydration of a disperse phase are a disproportionately great viscosity of the solution, a decreased activity of the movement of the particles as displayed in diffusion or in an electric field, and an alteration in volume or density in the direction of compression of the medium." Zsigmondy³ assumes that a density increase must be due to a compression of the particle by its water layer. A contraction in volume when gelatin is dissolved in water is then an evidence of hydration. The varying amount of water in gelatinous coagula shows hydration. Zsigmondy⁴ states that egg white and gelatin must have thicker layers of water than the non-soluble gold and that this assumption probably explains the stability of the former to addition of electrolytes. This exemplifies sols of the hydrophile and hydrophobe type. This author feels that this stability is due to the film of water rather than to the dispersion size of gelatin and gold. Remy also⁵ ascribes a shell of water (Wasserhülle) to the ions of salts in solution.

A high degree of hydration corresponds to a high viscosity in the sol according to Pauli⁶ and Hatschek.⁷ At the iso-electric point of gelatin, at PH about 4.7, a mini-

¹ This paper constitutes the major portion of a thesis submitted by Bruno A. Stein in partial fulfilment of the requirements for the degree of Master of Science at the University of Wisconsin.

² Pauli, "Colloid Chemistry of the Proteins," P. Blakiston's Son and Co., Philadelphia, 1922, p. 10.

³ Zsigmondy, "Kolloid Chemie," Otto Spamer, Leipzig, 1920, 3rd ed., p. 99.

⁴ Ref. 3, pp. 97-100.

⁵ Remy, Z. physik. Chem., 89, 467 (1915).

⁶ Pauli, ibid., 89, 529 (1915).

⁷ Hatschek, "Introduction to Physics and Chemistry of Colloids," J. and A. Churchill, London, 1922, 4th ed., p. 84.

mum viscosity is observed by Loeb, and it therefore would be also a minimum of hydration. At PH 3.0-3.2 there is a maximum hydration according to the same authority.

As stated above, Pauli explained the decrease in volume, or increase in density, since the two are reciprocal functions, when proteins are dissolved, by assuming hydration of the particles. We picture the particle surrounded by a shell of highly compressed water. Measurements of the density of gelatin sols should give a measure of the degree of hydration. It was thought that if density determinations over a range of Sörensen values should show a maximum for acids at PH 3.2, which corresponds to the point of maximum viscosity, then Pauli's hydration theory would be further verified.

Pauli and Handovsky have shown that salts in general have a depressing effect upon the viscosity of protein sols. This is also true for some organic substances. It was thus hoped to get at the hydration by means of variations in density with different concentrations of acids, salts, and non-electrolytes.

Experimental Part

Approximately $2\ N,\ N,\ 0.1\ N,\$ and $0.001\ N$ solutions of acids were prepared (it was not necessary to have the normality absolutely exact since the Sörensen values were determined later with the hydrogen electrode, these values being tabulated in Table II). Salt solutions were prepared to contain equivalent amounts of chlorine so that $0.1\ N$ sodium chloride contained one mole per liter while N strontium chloride contained 0.5 mole per liter. For the non-electrolytes such as dextrose or glycerol, N solutions were prepared that contained one mole per liter.

Density determinations were made on 5% gelatin solutions which were prepared in the following manner. The material used was a grade A1 gelatin intended for culture media. In order to obtain gelatin containing a constant amount of moisture regardless of humidity changes in the atmosphere, the stock material was dried for two and one-half hours in an electric oven at 50-60°. It was then broken into small bits by passing it through a food chopper. The ground gelatin was kept in a desiccator. For each sample 5 g. was weighed out and transferred into a dry Erlenmeyer flask; 100 cc. of the desired solvent was then measured into the flask with a buret. Solution of the gelatin was effected by holding the flasks at the temperature of the thermostat, 35.2°, and shaking them frequently. The densities were determined with the aid of the Ostwald modification of the Sprengel pycnometer, one arm of which was equipped with a ground-glass cap while the other arm was fitted with a glass tube having a small bulb and bent in the shape of an elbow. With the pycnometer thus fitted, it was entirely submerged in the constant temperature bath, only the tip

⁸ Loeb, "Proteins and Theory of Colloidal Behavior," McGraw-Hill Book Co., New York, 1922, pp. 195-231.

of the elbow tube extending above the surface of the water. The hydrogenion concentrations of the acids were determined by the hydrogen-electrode method using a potentiometer sensitive to 0.2 or 0.3 millivolt.

Method of Calculation

The volume of the pycnometer was determined in the usual way. The density difference, d, was arrived at quite directly: the difference in weight between the pycnometer plus the gelatin sol and the pycnometer plus the pure solvent was divided by the volume of the pycnometer. A concrete example taken from the results will make the statement clearer. For 5% gelatin solution in N hydrochloric acid we find,

N HCl solution + pyc. =
$$50.8212$$
 g,
N HCl + pyc. = 50.4740 vol. of pyc. (27.17565) = $d = 0.012776$
Diff. = 0.3472

An attempt was made to standardize the various steps in the determinations as much as possible. For instance, the time required to weigh out the gelatin was always about the same.

Data and Discussion of Results

Density-difference determinations were made using both electrolytes and non-electrolytes. The former group consisted of acids (acetic, nitric, hydrochloric, sulfuric, and phosphoric) and salts (chlorides of the alkali and alkaline earth metals); the latter group was composed of organic substances such as urea, glycerol, and alcohol. Table I gives the values of d for 5% gelatin in acids of various concentrations as shown.

Table I

The Effect of Acids on the Density Difference
5% gelatin at 35.2°

Conen.	Acetic	Nitrie	Hydrochloric	Sulfurie	Phosphoric
$rac{N}{2}$	0.01395	a	0.01237	0.01145	0.01304
ئے 1	.01440	0.01243	.01277	.01251	.01369
0.1	.01470	.01361	.01356	.01377	01441
0.001	.01470	.01425	.01448	.01435	.01465

 $[^]a$ 2 N Nitric acid coagulated the gelatin; therefore, no determination of the density could be made.

It will be seen that in all cases d increases as the normality becomes less, or as the solution becomes more nearly pure water. The value of d is 0.01443 when only distilled water is used. Apparently all values of d approach that for water, although the values for N, $0.1\ N$, and $0.001\ N$ acetic exceed it.

The hydrogen-ion concentrations of the acids were determined with the hydrogen electrode and are tabulated in Table II as Sörensen values.

Table II
THE SÖRENSEN VALUES OF THE ACID SOLUTIONS

Conen.	Acetic P _H	Hydrochloric Рн	Sulfurie PH	Phosphorie $P_{\mathbf{H}}$
2	1.86	0.03	0.48	1.00
1	2.17	0.45	0.51	1.23
0.1	2.71	0.90	1.07	1.60
0.001	3.55	2.10	2.51	2.67

In Fig. 1 are plotted the values of d on the y-axis against the PH values of the acids on the x-axis. The value of d for pure water is 0.01443 and is plotted at PH 5.4. The first observation is that the density increases with PH and comes to a maximum; the Sörensen value for this maximum is very near to 3.0. From the maximum at PH 3.0, the density curves drop toward a minimum, probably near the iso-electric point. The curves for the variation of density with hydrogen-ion concentration

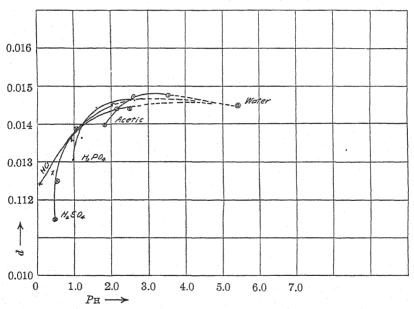


Fig. 1.—Effect of acids on d. The strength of the acids is expressed in Sörensen values would, therefore, in a measure be identical with those given by Loeb⁹ for the variation of total swelling, osmotic pressure, conductivity, and viscosity. The hydration of gelatin increases with the Sörensen value up to or near PH 3.0 as measured by the density of gelatin sols in various concentrations of acids.

If the density increase is due to the formation of a shell of highly compressed water around the gelatin particle, we should expect the density

Loeb, "Theory of Colloidal Behavior," McGraw-Hill Book Co., New York, 1922, p. 38.

to vary with the amount of acid in solution, since there is a contest set up between the gelatin particles and the acid for the possession of the water. ¹⁰ In Fig. 2 the values of d are plotted against the normality of the acids. When this is done, the acids fall (roughly) in the order of their strengths, the acetic and phosphoric coming above hydrochloric, nitric, and sulfuric. The hydration of the gelatin is not as much affected by acetic acid as by

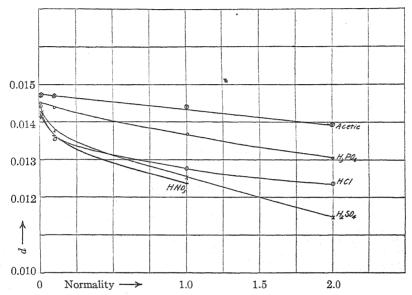


Fig. 2.—The effect of acids on d. The strength of the acid is expressed in normality sulfuric, for instance. From their positions on the graph, we may arrange these five acids in a series as regards their effect on the hydration of gelatin: acetic<phosphoric<hydrochloric<sulfuric and nitric.

In Table III are given the effects of salts on the density difference.

Table III
The Effect of Salts on the Density Difference
5% gelatin at 35.2°

Conen. N	LiCl	KCI	NaCl	CaCl ₂	SrCl ₂
2	0.01201	0.01037	0.01051	0.01004	0.00825
1	.01303	.01222	.01179	.01310	.01063
0.1	.01416	.01363	.01340	.01356	.01321
0.001	.01402	.01376	.01358	****	.01364

The values of d are of the same order as those obtained for the acids. On plotting d against the normality (with reference to the chlorine atom), in the same manner as for the acids, we get the curves of Fig. 3. The

¹⁰ Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft m. b. h., Leipzig, 1922, pp. 920–978.

value of d for gelatin in water for this series of runs is 0.01365 and is not plotted on the graph to avoid confusion. As the solutions become more dilute, the values of d approach that for pure water in all cases except lithium. It acts anomalously in that d for 0.1 N and 0.001 N solutions exceeds d for water. In the cases of these salts we again have evidence

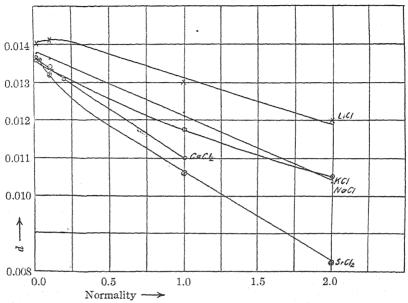


Fig. 3.—Effect of salts on d

of the hydration being affected by a contest between the gelatin and the salt for the possession of the water. An interesting point to note is that the curves for the chlorides of the alkali metals fall above those for the alkaline earth metals and in the order of their absorption on charcoal.¹¹ These cations can be arranged in a series with respect to their effect upon the density: Sr>Ca>Na,K>Li.

Similar density determinations were made on gelatin solutions with various concentrations of non-electrolytes, all organic substances including

TABLE IV

THE EFFECT OF NON-ELECTROLYTES ON THE DENSITY DIFFERENCE

507. relatin at 25.20

Conen.		o /o gerat			
N N	Dextrose	Urea	Glycerol	Methyl alc.	Ethyl alc.
2	0.01201	0.01312	0.01357	0.01485	0.01514
1	.01326	.01357	.01388	.01457	.01489
0.1	.01414	.01428	.01444	.01439	.01458
0.001	.01440	.01424	.01462	.01431	.01421

¹¹ Odén and Andersson, J. Phys. Chem., 25, 311 (1921). Osaka, Mem. Coll. Sci. Kyoto, 1, No. 6 (1915).

dextrose, urea, glycerol, methyl and ethyl alcohol. The results are given in Table IV, and shown graphically in Fig. 4. In general, the organic substances have much less effect on the hydration than do the acids and salts. A curious effect is obtained with the two alcohols: apparently their presence encourages the hydration of gelatin, since the density difference, d, increases with the increase in concentration of the alcohol. The slope of the curves is opposite in sign to those of the acids and salts.

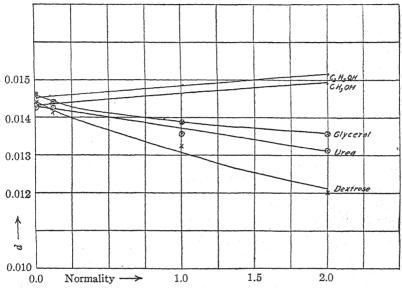


Fig. 4.—Effect of some organic substances

It is interesting to note in connection with the effect of salts and non-electrolytes on the density of the gelatin that Pauli and Handovsky¹² found that the viscosity of acid egg albumin was increasingly depressed by increased additions of salts such as sodium sulfate, sodium nitrate, sodium phosphate, and uranium nitrate. These same authors¹³ find that neutral salts depress the viscosity of alkaline egg albumin and that the salts of the alkaline earth metals are more effective than the salts of the alkali metals. Handovsky¹⁴ also finds that such organic substances as urea, caffeine, glycocoll, and aminobenzoic acid depress the viscosity of protein sols.

Summary

- 1. The variation in density of gelatin sols in different concentrations of acids was determined. It was found that for all the acids used, the den-
 - 12 Pauli and Handovsky, Biochem. Z., 18, 340 (1909).
 - 13 Pauli and Handovsky, ibid., 24, 239 (1910).
 - 14 Handovsky, ibid., 25, 518 (1910).

sity increases with an increase in hydrogen-ion concentration up to a maximum value at about PH 5.0, after which the density curves drop toward a minimum (probably coming at PH 4.7, although more data are necessary before a definite statement may be made).

- 2. The curves for the variation of viscosity of proteins with change in Sörensen values also have a maximum at PH 3.0–3.2 dropping to a minimum at the iso-electric point, PH 4.7, as shown by Loeb and Pauli. The similarity of the density curves to the viscosity curves adds further verification to Pauli's theory of hydration of proteins.
- 3. The acids may be arranged in a series as to their effect on hydration: acetic<phosphoric<hydrochloric<sulfuric<and<nitric.
- 4. It was shown that the effect of alkali and alkaline earth chlorides on hydration is of the same order as for acids and that the cations may be arranged in a series in the order of their effectiveness: Sr>Ca>Na,K>Li.
- 5. Non-electrolytes did not affect the hydration to nearly as great an extent as did the acids and salts. The anomalous action of methyl and ethyl alcohols seemed to indicate that they favored the hydration.

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[Contribution from the Bureau of Standards, United States Department of Commerce]

THE DETERMINATION OF TITANIUM BY REDUCTION WITH ZINC AND TITRATION WITH PERMANGANATE¹

By G. E. F. Lundell and H. B. Knowles

RECEIVED AUGUST 18, 1923

Introduction

Most texts leave the impression that the reduction of titanium by zinc in acid solution, as in a Jones reductor,² is a slow and difficult process. As a matter of fact, titanium is no more difficult so to reduce than iron³ and the reduction proceeds quickly and quantitatively to the trivalent stage.

The treatment of the reduced titanium solution is also usually made a matter of special precautions, such as catching the liquid in a measured excess of a standard permanganate solution or in an atmosphere of hydrogen or of carbon dioxide. Here, precautions are well taken, as trivalent titanium is very easily oxidized. The question, therefore, concerns the choosing of the most effective preventive and is answered by the use of

- ¹ Published by permission of the Director of the Bureau of Standards of the United States Department of Commerce.
- ² For details concerning the construction of a Jones reductor, consult such texts as Treadwell-Hall, "Analytical Chemistry," Vol. II, 5th Ed., J. Wiley and Sons, p. 638, or Scott, "Standard Methods of Chemical Analysis," Vol. I, 3rd Ed., p. 320.
- ⁸ W. F. Hillebrand in *U. S. Geol. Survey, Bull.*, 700, p. 169, calls attention to this fact and to a communication from Mr. J. A. Holladay, Chief Chemist of the Electro Metallurgical Co., on the same subject.

a solution of ferric sulfate in the receiving flask in the same way that was recommended by Randall⁴ for the determination of molybdenum. The use of permanganate in the receiver is unsatisfactory, as is generally recognized. The maintenance of an atmosphere of hydrogen or of carbon dioxide entails extra labor and expense and is desirable only when both iron and titanium have been reduced and a direct titration of titanium is desired, or when a titanous solution is wanted for volumetric work.

In view of the above remarks and of the increasing use of titanium in various products, it seems desirable to present the following data which demonstrate the ease with which titanium can be quantitatively reduced in a Jones reductor and quantitatively determined by catching the solution under ferric sulfate and then titrating with permanganate.

Experimental Part

A solution of titanic sulfate in sulfuric acid of 5% by volume was prepared from potassium titanium fluoride by repeated crystallizations of the salt, followed by evaporations with sulfuric acid. Tests demonstrated the absence of iron and zirconium and the solution was standardized both by precipitation with ammonia and by cupferron. With ammonia, three precipitations were made and the weighed oxide was freed from silica. The results obtained by the two methods agreed within 1 part in 2000. Weight burets were used in all of the work.

The reductions were made in a reductor having a bore of 19 mm. and a zinc column 43 cm. in length. Our experience has been that satisfactory reduction can be obtained in any reductor which provides a reasonable contact with amalgamated zinc. The reductor was always washed out with dil. sulfuric acid before runs in order to eliminate reducing compounds which are formed as the reductor stands idle. The usual reduction procedure was then followed and there were added in order, 25–50 cc. of dil. sulfuric acid 3–5% by volume, 150 cc. of the same solution containing the titanium, 100 cc. more of acid, and finally 100 cc. of water. The reduction was performed at a speed of approximately 100 cc. per minute or 4 minutes for the passage of all solutions through the reductor.

The reduced solution was caught under a 3-5-fold excess of ferric sulfate⁶

- ⁴ Randall, Am. J. Sci., [4] 24, 313 (1907).
- ⁵ Thornton, Am. J. Sci., [4] 37, 173, 407 (1914). Lundell and Knowles, J. Ind. Eng. Chem., 12, 346 (1920).
- ⁶ Randall (Ref. 4) and various texts prescribe the use of a solution of ferric ammonium sulfate. Our experience goes to show that a sulfuric acid solution of ferric sulfate prepared from ingot iron or plain carbon steel is preferable in that it is less expensive, the absence of ferrous salts and chlorides is assured, and the solution has a clearer color when used alone or with phosphoric acid. Such a solution is made by dissolving the material in aqua regia, evaporating to the fuming point with sulfuric acid, and diluting to proper volume after chlorides have been expelled; 0.02 g. of iron per cc. of 8% (by volume) sulfuric acid is a convenient strength and this will satisfactorily provide for 0.004 g. of titanium.

solution and then titrated with $0.1\ N$ permanganate which had been standardized against sodium oxalate. No phosphoric acid was used in the receiver because of the insolubility of titanium phosphate. All titrations were corrected by careful runs on the reagents and end-point.

The data are given in Table I.

Table I

The Reduction of Titanium by Zinc

Acidity of solution, 5%. All solutions were thoroughly boiled except where otherwise indicated

		muicateu		
Titar Taken G.	ium Found G.	Error G.	Reducing Temperature °C.	conditions Ferric iron used X theoretical
0.1108	0.1110	+0.0002	90-100	5
.0551	.0555	+ .0004	90-100	5
.0051	.0053	+ .0002	90-100	5
$.1052^{a}$.1053	+ .0001	90-100	5
$.0529^{a}$.0532	+ .0003	90-100	5
$.0059^{a}$.0058	— .0001	90-100	5
$.1022^{b}$.1024	+ .0002	22 - 25	5
$.0506^{b}$.0508	+ .0002	22 - 25	5
$.1025^{a,b}$.1028	+ .0003	22 - 25	5
.0999°	.1010	+ .0001	22 - 25	5
1053^{d}	.1056	+ .0003	75-80	5
$.1089^{d}$.1092	+ .0003	75-80	5
.1012	.0854	- .0158	90-100	None
$.0542^{a,b}$.0503	- .0039	22-25	None
.1063	.1045	0018	90-100	1
$.1074^b$.1062	0012	22-25	1
.1071	.1071	≠ .0000	90-100	3
$.1061^{b}$.1061	≐ .0000	22-25	3

^a Acidity of solution, 3%.

The data in Table I show that a rapid, quantitative reduction of titanium can be had in a Jones reductor, provided the reduced solution is caught under a solution containing at least three times more ferric salt than is necessary to oxidize the reduced titanium. The slight errors average no more than one drop of titrating solution and are undoubtedly due to experimental errors which could be largely eliminated if it were necessary to do so. The data also show that the reduction can be done with sulfuric acid of 3–5% by volume at any temperature between 25° and 100°, that it is not necessary to expel air from the solutions used in the reductor, and that an excess of ferric sulfate must be used in the receiving flask.

When titanium is reduced in the Jones reductor and then titrated as above, it should be borne in mind that the results will be in error if other reducible compounds are present. Such are: certain organic compounds, nitric acid, tin, arsenic, antimony, molybdenum^{III}, iron^{II}, chromium^{II}, vanadium^{II}, tungsten, uranium and columbium. Of these, the effect of

^e Solutions not boiled.

^b Solutions cooled after boiling.

^d Solutions quickly warmed.

the first five is indefinite and depends on experimental conditions; molybdenum, iron, chromium and vanadium are quantitatively reduced to the valences which are indicated; the reduction of the last three is not definite. tungsten approaching the quinquevalent, and uranium and columbium the trivalent state. The list seems large and formidable, but in reality it is not so. Some of the compounds are uncommon and all, save columbium. can be removed with but little effort. For example, it is obvious that nitric acid can be easily removed by evaporations with sulfuric acid and that organic compounds can be destroyed by evaporation with the same acid together with oxidizing agents such as nitric, permanganic or persulfuric acids. The simple remedy for tin, arsenic, antimony and molybdenum is, of course, treatment with hydrogen sulfide in a solution sufficiently acid to prevent hydrolysis of titanium. The elimination of iron is a little more laborious, as it involves three treatments: reduction of the iron by hydrogen sulfide in acid solution, its precipitation by ammonium sulfide in the presence of tartrate, and the removal of the tartrate as outlined above. The separation of titanium from chromium, vanadium, tungsten and uranium is conveniently done by filtration after oxidation in alkaline solution as, for example, with sodium carbonate and sodium peroxide: in this separation, it is to be borne in mind that at first titanium is also oxidized and rendered soluble and that thorough boiling of the solution is necessary to effect its complete precipitation. It is fortunate that columbium is rarely met, as its separation from titanium is a difficult

In conclusion, it is interesting to record that the preparation of titanous solutions for use in volumetric work should not be much more difficult than the task of preparing the corresponding titanic solutions. This follows because any volume of the acidified titanic solution can be run through a Jones reductor and caught in a bottle of suitable size fitted with a 3-hole stopper carrying the outlet of the Jones reductor, and inlet and outlet tubes for maintaining the necessary neutral atmosphere of carbon dioxide or hydrogen.

Summary

The reduction of titanium in a Jones reductor proceeds rapidly and is quantitative, provided the reduced solution is caught under a 3-5-fold excess of ferric sulfate.

The reduction is conveniently carried on in solutions containing 3-5% by volume of sulfuric acid and may be done at any temperature between 25° and 100° .

Attention is called to interfering compounds and their removal, and to the ease with which titanous solutions can be prepared for volumetric use.

Washington, D. C.

[Contribution from the Chemical Laboratory of Clark University, No. I, 32]

STUDIES RELATING TO METALLO-ORGANIC COMPOUNDS. I. INTRODUCTION. II. THE EQUIVALENT CONDUCTANCE OF TRIMETHYLSTANNYL CHLORIDE IN ETHYL ALCOHOL

By Charles A. Kraus and Conral C. Callis Received September 8, 1923

Introduction

The metallo-organic compounds, that is, compounds in which metallic elements appear united with carbon groups, have attracted marked attention within recent years after having passed through a long period of neglect. But even now efforts are directed chiefly towards the preparative side, while the physicochemical properties of these compounds remain largely undetermined. It might be expected that in the metallo-organic compounds the metallic elements function in a manner analogous to carbon in ordinary carbon compounds and that here, if anywhere, substances might be formed which should serve to bridge the gap between inorganic and organic compounds. The present series of investigations was undertaken for the purpose of supplying further knowledge in this field, particularly in relation to the constitution and physicochemical properties of certain of these compounds.

The metallo-organic compounds may be divided into several classes: first, the derivatives of the normal elements of the fifth, sixth and seventh groups; and second, the derivatives of the normal elements of the first, second, third and fourth groups and of certain of the heavier elements of other groups.

The members of the first class of substances are, in general, more stable than those of the second. They may be looked upon as organic derivatives of the normal hydrides of the elements in question, although the hydrides, as a rule, are much less stable than the corresponding organic derivatives.

The elements of this group form mixed compounds in which the valences of the central element may be partially satisfied by hydrogen and partially by hydrocarbon groups. Other mixed compounds may also be formed in which a portion of the valences may be satisfied by electronegative elements or groups. These latter compounds are not, as a rule, very stable, particularly with respect to water, which hydrolyzes them readily. They do not appear to possess salt-like properties in a marked degree. Some of the elements of this group are metallic and others non-metallic and there is nothing to indicate that any marked distinction exists between compounds derived from metallic and those derived from non-metallic elements.

A remarkable property of the members of this group of substances is their power of combining with acids and with the organic halides to form stable compounds of the formula $M''R_{n+1}$ X, in which n is the normal

valence of the element with respect to hydrogen, R is a univalent organic group or hydrogen, and X is an electronegative element. These compounds, which are well known, being represented by the substituted ammonium, sulfonium and iodonium salts, exhibit marked electrolytic properties, in that they are highly ionized in water as well as in practically all other solvents of higher dielectric constant, are conductors of electricity in the fused condition, and yield strong bases. Thus, the substituted ammonium, sulfonium and iodonium bases, as well as the bases of other elements of these groups, are practically as strong as the hydroxides of the alkali metals.

The second group of compounds, derived from the elements of the first, second, third and fourth groups, as well as from certain other heavy elements, may likewise be looked upon as organic derivatives of the hydrides of these elements. But while the hydrides have a relatively low stability, particularly in the case of the less electropositive elements, the corresponding organic derivatives are comparatively stable. These may be divided into two sub-groups, depending upon whether the element in question is strongly electronegative or strongly electropositive. In the case of the strongly electropositive elements such as sodium, the compounds are solids at ordinary temperatures, and exhibit, to some degree at least, electrolytic properties resembling those of the corresponding hydrides in this respect.1 The corresponding compounds of the less electronegative elements are, as a rule, mobile liquids at ordinary temperatures, having low freezing points and exhibiting no electrolytic properties. In a few instances mixed compounds are known in which hydrogen and organic groups both occur. In many instances, too, mixed compounds containing organic groups and strongly electronegative elements or groups of elements are formed, many of which are comparatively stable. However, those compounds containing two or more electronegative elements or groups show a considerable tendency to hydrolyze in the presence of water or other similar solvents.

The most interesting representatives of this series of compounds are those corresponding to the formula $M^nR_{n-1}X$, in which a single valence of the central element is satisfied by a strongly electronegative element or group. These compounds have ordinarily been looked upon as salts, and indeed they exhibit numerous properties common to salts. Thus, solutions of these compounds in water or the alcohols conduct the electric current, while they yield corresponding bases of the type $M^nR_{n-1}OH$, which exhibit marked alkaline properties in aqueous solution. It should be pointed out, however, that these bases are weak when compared with bases of the

¹ Hein, Z. Elektrochem., 28, 469 (1922).

² (a) Bredig, Z. physik. Chem., 13, 303 (1894). (b) Zelinsky and Krapiwin, ibid., 21, 47 (1896).

type M''R_{n+1}OH. Thus, the ionization constant^{2a} of trimethyl tin hydroxide at 25° is 1.7×10^{-7} .

While the compounds of the type $M^nR_{n-1}X$ have ordinarily been classed among the electrolytes or the salts, their behavior, even in solution in various solvents, would appear to indicate that they are not true salts. Thus Zelinsky and Krapiwin have determined the equivalent conductance of triethyl tin iodide in methyl alcohol²⁶ and have found that the solutions are not as highly ionized as are the corresponding solutions of typical salts, while at the same time they conform approximately to the law of mass action. The same is true of diethyl tin di-iodide in the same solvent, which here, however, appears to behave like a binary electrolyte.

The physical properties of the pure compounds do not correspond with those of salts. The mere fact that most of these substances have comparatively low melting points and are comparatively volatile at ordinary temperatures would appear to indicate that they are not true salts. Perhaps the most typical example of substances of this type is trimethyl tin iodide, which is a liquid boiling at about 170° and melting slightly above 0°. The properties of the corresponding bromide and chloride are similar to those of the iodide, the boiling points being somewhat lower and the melting points somewhat higher.

These compounds are characterized by their ready solubility in a great variety of liquids. At ordinary temperatures, trimethyl tin iodide, for example, is miscible (in all proportions) with water, alcohol, ether, acetone, petroleum ether, benzene, toluene, etc. Only in the case of ammonia and various amines does a solid phase appear. In this case, the solid phase consists of a compound between trimethyl tin iodide and the solvent. The nature of the compound here involved will be discussed more fully subsequently.

Compounds of this class do not conduct the electric current in the pure liquid condition. Thus the specific conductance of trimethyl tin iodide is below 0.3×10^{-5} . What the true value of the conductance of this substance is cannot readily be determined, owing to the fact that traces of impurity have a strong influence on its conductance and the purification of these substances is not readily accomplished. The other halides of the trimethyl tin group exhibit properties corresponding to those of trimethyl tin iodide. So, also, amyl mercury iodide in the fused state is a poor conductor of the current. It is probable that all substances of this type are non-electrolytes in the fused condition.

In solution in various solvents the compounds of this type exhibit marked divergence from ordinary salts. In Table I are given approximate values of the conductance of trimethyl tin iodide in different solvents.

An examination of this table will show that while trimethyl tin iodide conducts the current fairly readily in certain solvents, in other solvents it is virtually a non-conductor. Furthermore, there is no relation between the conductance of the solutions and the dielectric constant of the solvent medium. Thus the conductance in nitrobenzene and nitromethane, of dielectric constants 36 and 39, respectively, is little higher than that in ether or benzene. In other words, dissolved in these solvents, trimethyl tin iodide is not an electrolyte. On the other hand, in acetone, pyridine, and the alcohols, trimethyl tin iodide conducts the current fairly readily.

Table I Conductance of Trimethyl, Tin Iodide in Various Solvents Specific cond. of (CH3)3SnI = 0.3×10^{-5} .

01 (0113)	30117 - 0.6	, , , 10 .	
Dielectric const.	Dilution	Specific cond.	Equiv. cond.
2.3	0.271	2.21×10^{-6}	
4.4	0.677	1.27×10^{-5}	
. 36	0.948	1.02×10^{-5}	
. 39	0.948	5.70×10^{-5}	
. 26	0.271	1.58×10^{-4}	
8.8	0.406	3.68×10^{-6}	
6.1	0.406	7.37×10^{-5}	
. 22	0.271	4.42×10^{-3}	0.120
	92.5	2.48×10^{-5}	0.229
. 16	0.271	1.44×10^{-2}	0.390
	8.67	5.84×10^{-5}	0.503
. 13	0.271	8.86×10^{-2}	2.40
	8.67	3.81×10^{-3}	3.30
. 13	0.215	7.03×10^{-2}	1.51
	13.72	1.92×10^{-3}	2.65
. 26	0.271	4.41×10^{-2}	1.20
	1.084	2.22×10^{-2}	2.41
	Dielectric const. 2 .3 .4 .4 .4 .36 .39 .26 .8 .8 .6 .1 .22 .16 .13 .13	Dielectric const. Dilution 2.3 0.271 4.4 0.677 36 0.948 39 0.948 26 0.271 8.8 0.406 22 0.271 92.5 16 0.271 8.67 13 0.271 13 0.215 13.72 26 0.271 0.271	Dielectric const. Dilution Specific cond. 2.3 0.271 2.21 × 10 ⁻⁶ 4.4 0.677 1.27 × 10 ⁻⁵ 36 0.948 1.02 × 10 ⁻⁵ 39 0.948 5.70 × 10 ⁻⁵ 26 0.271 1.58 × 10 ⁻⁴ 8.8 0.406 3.68 × 10 ⁻⁶ 6.1 0.406 7.37 × 10 ⁻⁵ 22 0.271 4.42 × 10 ⁻³ 92.5 2.48 × 10 ⁻⁵ 16 0.271 1.44 × 10 ⁻² 8.67 5.84 × 10 ⁻⁵ 13 0.271 8.86 × 10 ⁻² 8.67 3.81 × 10 ⁻³ 13.72 1.92 × 10 ⁻³ 13.72 1.92 × 10 ⁻³ 26 0.271 4.41 × 10 ⁻²

the ionization in general being higher, the higher the dielectric constant of the medium, with the exception of acetone, in which solvent the conductance is markedly lower than even in amyl alcohol although the fluidity of acetone is much higher than that of amyl alcohol. It would appear that the electrolytic properties of solutions of trimethyl tin iodide are due to some specific interaction with the solvent medium. Apparently, those solvents containing basic oxygen or nitrogen atoms form electrolytic solutions. On the other hand, solvents which do not contain basic oxygen or nitrogen atoms yield non-conducting solutions, irrespective of the value of the dielectric constant.

It may be surmised that the electrolytic properties of solutions in the amines and the alcohols and similar compounds are due to the formation of compounds of the ammonium and oxonium type. That this is actually the case will be shown in other numbers of this series.

The Equivalent Conductance of Trimethyl Tin Chloride in Ethyl Alcohol

The work of Zelinsky and Krapiwin, as well as our own preliminary measurements, indicates that the trimethyl tin halides are ionized in

Fig. 1

alcoholic solution, although less than are the corresponding typical salts. It appeared of interest to determine the true degree of ionization of one of these compounds in alcohol, as well as to determine whether or not the law of mass action is here applicable.

Materials and Apparatus.-Trimethyl tin chloride was prepared by chlorinating tin tetramethyl which had previously been purified by treating with ammonia vapor to precipitate any halide present, leaving behind the tin tetramethyl.3 Chlorination is readily effected by leading dry chlorine through tin tetramethyl cooled in ice water with the exclusion of daylight. The trimethyl tin chloride is separated from any excess tin tetramethyl by fractional distillation and is finally purified by successive recrystallizations from low-boiling petroleum ether at low temperatures. The last traces of petroleum ether are removed by means of a vacuum pump.

Trimethyl tin chloride crystallizes in the form of needles melting at 37°.

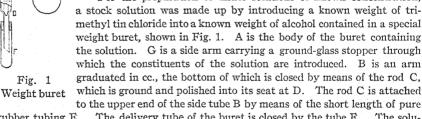
Absolute alcohol was prepared by dehydrating 95% alcohol with lime in the usual way. This product was then treated with freshly dehydrated copper sulfate, 1 kg.

of copper sulfate for 6 liters of alcohol, the whole being heated under a reflux condenser for several days, with a slow stream of air passing through the apparatus. The alcohol was then vaporized with a stream of pure dry air passing through it; about 3/4 of the vapor was condensed and collected for use, the remainder passing by and being later condensed and rejected. By this method, alcohol having a specific conductance of 3.0×10^{-8} was obtained.

The conductance apparatus and thermostat employed were similar to those earlier employed in this Laboratory and described elsewhere in THIS JOURNAL.4

The cell employed was that previously used by Kraus and Kurtz⁵ in this Laboratory; its constant was found to be 0.018286 ± 1 . measurements were carried out at 25.00 ± 1°.

For the preparation of dilute solutions of known concentration, graduated in cc., the bottom of which is closed by means of the rod C,



rubber tubing E. The delivery tube of the buret is closed by the tube F. tion in the buret at no time comes in contact with a lubricated surface. Approximately the desired amount of solution is introduced into the side arm B, after which the end of the buret is introduced into the cell and the liquid in B is allowed to run out by raising the rod C. When all the liquid has run out, the buret is removed from the cell and the cap F replaced, and the amount of solution introduced into the cell is determined by reweighing the buret. This apparatus has been found extremely useful in handling liquids which dissolve stopcock lubricant.

The cell was removed from the bath after each addition of solution, and the contents were thoroughly mixed. The cell was then returned to the thermostat and conductance

³ Werner and Pfeiffer, Z. anorg. Chem., 17, 82 (1898).

⁴ Kraus and Parker, This Journal, 44, 2429 (1922).

⁵ Kraus and Kurtz, ibid., 44, 2463 (1922).

measurements made at intervals until a constant value was reached. This procedure was repeated until check readings were obtained. At the lower concentrations, a slow change in the value of the conductance took place with time, which rendered these observations somewhat uncertain. At higher concentrations, this effect was not observed; it was greatly accentuated in case the specific conductance of the alcohol was high. In the case of the iodide the effect was much more pronounced than in that of the chloride and could not be overcome at the time.

Experimental Results.—In Table II are given the results of a series of measurements with trimethyl tin chloride at 25° . The specific conductance of the solution given in the second column has been corrected for the specific conductance of the solvent, whose value is given at the head of the table. The equivalent conductance is given in the third column and the mass-action function, $K \times 10^4$, in the last column.

Table II Conductance of Trimethyl Tin Chloride in Absolute Alcohol at 25° 347.37 g. of absolute alcohol. Specific conductance, l, of alcohol = 0.305×10^{-7} . Cell constant, 0.018286. Solution added contained 4.83% of (CH₃)₃SnCl by weight

Conen. × 103	Specific Cond. $l \times 10^7$	Equivalent cond. Λ	$K \times 10^4$
0.1566	17.88	11.42	0.346
0.2600	24.16	9.29	.344
0.3178	27.56	8.67	.356
0.6219	40.09	6.45	.350
1.0441	53.36	5.11	.349
1.8773	72.91	3.89	.347
3.0545	94.55	3.10	.349
4.9749	122.58	2.46	.350
8.9449	167.47	1.87	.356
16.5707	234.09	1.41	.369

Discussion.—The results are shown graphically in Fig. 2, values of $1/\Lambda$ being plotted as ordinates and values of the specific conductance as abscissas. If the law of mass action is applicable, the experimentally determined points, according to this plot, should lie on a straight line, the intercept of which on the axis of ordinates yields the value of $1/\Lambda_0$ and the slope of which gives the value of K/Λ_0^2 , from which the value of K may be determined.

An examination of the plot will show that, with the exception of two or three determinations at higher concentrations, the points lie on a straight line practically within the limits of the experimental error. This is also indicated by the value of the mass-action constant as given in the last column of Table II. The plot yields for Λ_0 the value 30.8, and for K the value 0.349×10^{-4} .

It is evident that the law of mass action holds very nearly up to a concentration of 10^{-3} equivalents per liter, while at higher concentrations there is a slow deviation in the same direction as in the case of ordinary electrolytes in solvents of higher dielectric constant. This electrolyte in

alcohol, therefore, resembles moderately weak acids and bases in water and moderately strong acids in alcohol. This is a striking fact, inasmuch as it is practically the first instance of an electrolyte, other than an acid or a base, which has been shown to conform to the law of mass action in solvents of higher dielectric constant.

Heretofore, the only weak electrolytes known have been the acids and bases. It appears, however, that, in general, compounds of the type $M^nR_{n-1}X$ are comparatively weak electrolytes.

Actually, the compounds of this type have many properties in common with the acids. As has already been pointed out, in the pure liquid state they are indifferent conductors of the electric current. In solution they

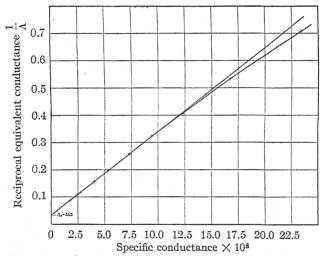


Fig. 2.—Approach of conductance values to the mass-action relation of solutions of $(CH_3)_3SnCI$ in absolute alcohol

act as electrolytes only when dissolved in solvents of the basic type, such as ammonia, water, etc. This is also true of the acids. In the case of the acids, the conductance is accounted for on the assumption that a compound of the type $M^nH_{n+1}X$ is formed between the acid and the solvent. As will later be shown, the compounds of the type $M^nR_{n-1}X$ likewise combine with solvents of the ammonia and water type to form new compounds of the type $M^nR_{n+1}X$. These compounds, therefore, so far as their physicochemical properties are concerned, may be classed with the acids.

That this should be the case is not unexpected, as has been pointed out by one of the authors.⁶ The behavior of an element, or a group of elements, in its compounds with other elements or groups, is determined by its position in the potential series. A strongly electropositive group combined

⁶ Kraus, Rec. trav. chim., 42, 588 (1923).

with a strongly electronegative element or group yields an electrolyte, that is, a compound which is ionized in the pure state as well as in solution. As the electropositive constituent becomes less electropositive, the electrolytic properties of the resulting compound become less pronounced, the specific conductance of the pure substance in the liquid condition diminishes and its ionization in solution, under otherwise comparable conditions, likewise diminishes. When the electropositive constituent lies somewhere near the middle of the potential series, in other words, when its position corresponds with that of hydrogen, the compound will exhibit practically no electrolytic properties, or only weakly electrolytic properties in the pure state and, in general, will not exhibit electrolytic properties in solution. Only in case the group is capable of associating itself with the solvent, or some added substance, to form a new and more electropositive group will solutions of these compounds exhibit electrolytic properties.

That a group of the type of the trimethyl tin group lies intermediate in the potential series is further shown by the fact that this group forms a stable negative as well as positive ion. In fact, compounds in which this group acts electronegatively are probably true salts. Thus, compounds of the type (CH₂)₃SnNa may readily be formed, and these compounds exhibit marked electrolytic properties in solution and in general behave like salts. Such compounds will be discussed more fully in a succeeding article.

Summary

- 1. The metallo-organic compounds corresponding to the formulas $M^nR_{n+1}X$ and $M^nR_{n-1}X$ exhibit electrolytic properties, but only the members of the first class are true electrolytes. The members of the second class exhibit electrolytic properties only under particular conditions.
- 2. Data are given for the conductance of trimethyl tin iodide in the pure state and in solution in various solvents. The pure compound is a poor conductor, while solutions of this compound in solvents of the non-basic type are likewise poor conductors, even though the dielectric constant of the solvent may be high. Solutions in the alcohols and the amines are relatively good conductors.
- 3. The equivalent conductance of trimethyl tin chloride in absolute alcohol at low concentrations has been measured. From these measurements the value 30.8 is deduced for Λ_0 . Up to a concentration of 10^{-2} N, the conductance values conform to the law of mass action within the limits of the experimental error. The mass-action constant has the value 0.349×10^{-4} .
- 4. The properties of compounds of the type of trimethyl tin chloride are discussed. It is suggested that the electrolytic properties of solutions of this and similar compounds in the alcohols and the amines are due to

the formation of a more electropositive group by combination of the trimethyl tin group with the solvent. It is pointed out that the properties of trimethyl tin chloride correspond closely to the properties of methyl iodide and more particularly to those of the halogen acids.

5. The properties of the trimethyl tin group and of its compounds may be accounted for on the basis of the electro-affinity of this group. The analogy which this group bears to hydrogen is pointed out.

Worcester, Massachusetts

[Contribution from the Gates Chemical Laboratory of the California Institute of Technology, No. 32]

THE FREE ENERGY AND HEAT OF FORMATION OF LEAD MONOXIDE

By David F. Smith¹ and Hubert K. Woods Received September 11, 1923

Introduction

The purpose of this investigation was to determine the change in the free energy and heat content when lead oxide (PbO) is formed from its elements at 25°.

Apparently no measurements have yet been made from which the free energy of lead oxide may be accurately obtained. High-temperature equilibria would doubtless be complicated by the formation of other oxides of lead and always involve a more or less unreliable extrapolation to standard temperature on account of inaccurate heat data. Lewis and Randall² have attempted to calculate the free energy of lead monoxide from solubility measurements and molal free energies but obtain a very uncertain value. As the results of Berl and Austerweil³ show, in solutions of lead monoxide there is considerable formation of complex ions such as PbOH+, so that the activity of the lead ion would be difficult to estimate even in very dilute solutions. Lewis and Randall² have also pointed out the probable uncertainty in the thermochemical value of the heat of formation of lead monoxide and the excessive discrepancy between their approximate value of its free energy and that obtained by using low-temperature specific-heat data, heats of reaction, and the constant entropy principle (the so-called "third law of thermodynamics").

Since lead oxide is only slightly soluble in dilute alkaline solutions, a measurement of the electromotive force of cells such as $H_2(g)$ | dil. alkaline solution | PbO(s) + Pb(s) should give directly a measure of the free-energy change in the reaction $H_2(g)$ + PbO(s) = Pb(s) + H_2 O(l). A combina-

¹ National Research Fellow in Chemistry.

² Lewis and Randall, "Thermodynamics," McGraw-Hill Co., New York, 1923, p. 497.

³ Berl and Austerweil, Z. Elektrochem., 13, 165 (1907).

tion of the electromotive-force measurements with the known value of the free energy of liquid water would give the free-energy content of 1PbO(s).

In view of the unreliability of the thermochemically determined heat of formation, we have obtained the heat of the above reaction from the temperature coefficient of the electromotive force of the above-mentioned cells. This, when combined with the known heat of formation of liquid water, gives the desired heat of formation. The possession of the requisite low-temperature specific data, together with the free energy and heat of formation of lead oxide permits a further test of the "third law."

This research was carried on in part with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington, for which the authors wish to express their indebtedness.

Preparation of Materials and Solutions

We prepared for use in our cells red lead monoxide, which is the stable form at ordinary temperatures.⁴ The yellow oxide and also the hydroxide, in contact with alkaline solutions, slowly change over to the stable red form. A fine, crystalline, dark red oxide was obtained by slowly adding crystals of pure lead acetate to a boiling, concentrated solution of sodium hydroxide from which the carbonate had been removed by the addition of a small amount of barium hydroxide. The oxide thus obtained was thoroughly washed with water and dried in a vacuum over sulfuric acid.

Lead was plated on platinum spirals from a solution of pure lead oxide in strong perchloric acid containing a small amount of Witte's peptone. This gave a light gray, closely-adhering deposit free from occlusions. Finely divided lead was prepared by fusing pure lead carbonate with pure sodium cyanide in a porcelain dish, and filing the button thus obtained.

Barium hydroxide solution was used as electrolyte, since it is more easily obtainable pure than are the alkali hydroxides and also because it remains free from dissolved carbonate. The solution was made from a high grade of the pure crystallized salt of commerce.

Air was carefully excluded from all solutions and from the cell by the use of glass flasks fitted with sealed-on outlet tubes and connected to a supply of nitrogen.

Apparatus

One of the chief difficulties experienced with cells which depend upon the saturation of a solution with a solid lies, we believe, in the slowness of the approach to saturation and of the removal of oxygen. This can, however, be obviated by efficient stirring of the solution. We have, therefore, used an automatic pump which saturates and stirs the solution di-

⁴ For a discussion of the relative stabilities of the various forms of lead oxide, their solubilities, etc., see Abegg, "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, 1909, III [2] 673 ff. and 677 ff.

rectly in the cell without contact of the solution with air or with other than glass apparatus.

The complete cell, with the circulating pump attached, is shown in Fig. 1.

Referring to the diagram, the glass tube CC is fitted with an inner tube BB in which slides a loosely-fitting plunger P consisting of strips of transformer iron completely enclosed in a glass tube. When the electromagnet AA is energized (by an automatic current-interrupter not shown in the figure) the glass plunger P rises rapidly, forcing the liquid which completely fills the interior of the apparatus, up through the inner tube and down the annular space between CC and BB, out at D, through the glass wool plug E, through the mass of lead and lead oxide at F, out again through the glass wool plug at the top and side of the lead cell T, opening the float valve H which is ground to a seat

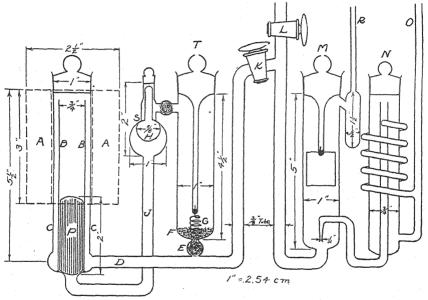


Fig. 1

at S, down the tube J and back to the bottom of the plunger P. The current through the electromagnet having been broken, the plunger P slowly sinks to the bottom of the tube BB allowing the solution to pass between it and the walls of the tube, the reseating of the float valve H preventing backward flow of the liquid. The cycle is repeated at intervals of 5 or 6 seconds, pumping about 6 cc. of solution per stroke. In a short time this whole section of the apparatus is filled with a fine silt of the oxide which exposes a large surface and quickly saturates the solution.

The hydrogen saturator and half-cell are shown at the extreme right of the figure. The hydrogen, entering at O, passes around the spiral in small bubbles which emerge from the top of the spiral, the solution returning to the reservoir N and the gas passing through the central tube and into the hydrogen cell M. This type of saturator gives long contact of the gas with the liquid, avoids spray, circulates the solution in the reservoir, and offers little back pressure to the hydrogen generator. The trap at the bottom of the outlet tube R prevents moisture condensed from the escaping hydrogen from flowing back into the cell.

The hydrogen for the cell was generated by electrolysis of a potassium hydroxide solution contained in a U-tube, the oxygen electrode of which was placed well up in the side arm to prevent diffusion of oxygen over to the hydrogen side. The hydrogen passed over a platinum coil electrically heated to redness to remove traces of oxygen, and over phosphorus pentoxide to remove water, then through a fine capillary tube which regulated the flow of hydrogen through the saturator and cell.

The cells were kept in a bath of light oil (commercially known as "Transil Oil"), the temperature remaining constant to 0.02° as determined by a thermometer calibrated by the Bureau of Standards.

The electromotive forces were measured with a potentiometer of a modern type against a Weston standard cell.

Measurement of the Electromotive Forces

We were careful to avoid the use of the lead obtained by electrolysis in the form of "lead tree," since this type of deposit is hard to wash free from traces of impurities and doubtless contains much occluded salt from the electrolyzing bath. The presence of carbonate is also undesirable, for although lead carbonate is very slightly soluble in water, it is doubtless somewhat soluble in alkaline solutions. Thus, when lead acetate solution was added to a solution of commercial sodium hydroxide there was no precipitate of lead carbonate, while barium carbonate precipitated in considerable amount when a solution of barium hydroxide was added.

The individual cells were run for a period of several days. They showed variations of less than 0.1 mv. for many hours after the cells had come to equilibrium. Each cell was alternately pumped out and allowed to stand until finally further pumping produced no change in the measured electromotive force.

The lead half-cell contained an excess of solid lead oxide mixed with finely divided lead, contact with which was made through platinum leads plated with lead as previously described.

Final values of the measured electromotive forces are presented in Table I. The headings are for the most part self-explanatory. The

TABLE I
OBSERVED ELECTROMOTIVE FORCES

		· ODDALK!	~~ ~~~~~		re out to	
Cell	Temp. °C.	Moles Ba(OH) ₂ per kg. H ₂ O	Pressure of hydrogen	E.m.f. obs.	E.m.f. when H ₂ is 1 atm.	Best value
1	25	0.2242	722	0.2487	0.2494	
2	25	.0766	722	.2487	.2494	
3	25	.2478	721	.2487	.2494	
4	25	.1488	724	.2486	.2492	0.2494
5	45	.2242	673	.2414	.2431	
6	45	.0766	674	.2412	.2429	
7	45	.2478	672	.2416	.2433	
8	45	.1488	676	.2414	.2430	0.2430

hydrogen pressure given has been corrected for the observed barometer reading, the vapor-pressure of water at the respective temperatures, and a head of 1 or 2 cm. of water above the electrodes in the hydrogen half-cell. Each value of "e.m.f. observed" is the value obtained for a separate filling of the cell with new solution and materials.

Calculations

From the "best values" of our electromotive forces we find for the reaction PbO(s) + H₂(1 atm.) = H₂O(l) + Pb(s) the following free energy values: at 298.1° K., $-\Delta F = 11,509$ cal.; at 318.1° K., $-\Delta F = 11,214$ cal. Taking the free energy of H₂O(l) at 298.1° K. as -56,560 cal., we calculate the free energy of PbO(s) at this temperature to be -45,050 cal. The difference between the free energy of pure water and that of water in the barium hydroxide solutions is hereby neglected; but this is permissible, since the vapor pressure of even a 0.25 molal solution certainly does not differ from that of water by more than 2%; and this corresponds to a free-energy difference of only 12 calories.

This free energy of lead oxide differs by about 4000 cal. from the value (—41,000 cal.) previously derived by Lewis and Randall from available solubility data for lead oxide and the electrode potentials of lead and oxygen.

Using the integrated Gibbs-Helmholtz equation, $\frac{E_2}{T_2} - \frac{E_1}{T_1} = \frac{\Delta H}{NF} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

whereby ΔH is assumed constant over the temperature interval involved (ΔC_p is only 6.0 cal. per degree), and substituting our measured electromotive forces, and the temperatures 318.1° and 298.1°, we calculate ΔH for the above reaction to be equal to —15,910 cal. Taking the heat content of liquid water at 25°C. to be —68,270 cal., 6 we calculate the heat of formation of PbO(s) from its elements at 25°C. to be —52,360 cal.

To obtain ΔH as a temperature function, this value of the heat of formation of 1 PbO at 25° may be combined with the following expressions for the heat-capacities at constant pressure: for 1 Pb, 6.01 + 0.00085 T + 0.00000154 T^2 ; for 1 PbO, 11.58; for $1/2O_2$, 3.25 + 0.0005 T. The expression for 1 Pb is derived from the values of the specific heats, 0.03083 at 18° and 0.03155 at 100°, obtained by Jaeger and Diesselhorst⁷ and the value 0.03380 at 300° obtained by Naccari.⁸ The expression for 1 PbO is derived from the value of the specific heat 0.0519 at 23° obtained by Russel,⁹ and that for $1/2O_2$ is taken from Lewis and Randall.¹⁰ These lead to the following expressions for the heat-content and free-energy increases ac-

⁵ Ref. 2, p. 485.

⁶ Ref. 2, p. 477.

⁷ Jaeger and Diesselhorst, Wiss. Abh. Phys.-Techn. Reichsanst., 3, 269 (1900).

⁸ Naccari, Atti acad. sci. Torino, 23, 107 (1887-88).

⁹ Russel, Phys. Z., 13, 59 (1912).

¹⁰ Ref. 2, p. 80.

companying the formation of 1 PbO from its elements at temperatures between 0°C., and the melting point of lead (327°C.):

$$\Delta H = -52,980 + 2.32 \ T - 0.000675 \ T^2 - 0.000000257 \ T^3$$

 $\Delta F = -52,980 - 2.32 \ T \ln T + 0.000675 \ T^2 + 0.000000128 \ T^3 + 39.62 \ T$

Lewis and Randall (Ref. 2, p. 497) give the value of $T\Delta S$, calculated from low-temperature specific-heat data with the aid of the constant entropy principle for the reaction Pb + $^{1}/_{2}O_{2}$ = PbO at 25°C. as —6900 cal. Subtracting this value from our value for the heat of formation of lead oxide we calculate the free energy of lead oxide at 25° to be —45,460. This value is 410 cal. less than the more accurate value based upon our electromotive-force measurements; but this is about the usual order of agreement between the free-energy value calculated upon the assumption of the constant-entropy principle and that obtained by chemical methods. 11

Summary

- 1. An apparatus has been described for effectively saturating and stirring the electrolyte in a cell, thereby decreasing greatly the time taken for a cell containing a solid salt to come to equilibrium.
- 2. Electromotive-force measurements upon the cell, $H_2(g) \mid Ba(OH)_2$ (0.0766–0.2242 M) | PbO(s) + Pb(s), give the free energy of PbO(s) as —45,050 cal. at 25°, when the free energy of liquid water at this temperature is taken as —56,560 cal.
- 3. From the temperature coefficient of the electromotive force of this cell the heat of formation of PbO(s) at 25° is calculated to be —52,360 cal. when the heat of formation of liquid water at 25° is taken as —68,270 cal. Temperature-functions for its heat-content and free energy have been derived.
- 4. From the above value for the heat of formation of PbO(s) and the value of its entropy of formation derived by Lewis and Randall from the constant-entropy principle, the free energy of PbO(s) at 25° is found to be —45,460 cal., which is as close to our more accurate experimental value as are most of the free energies computed by this method.

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¹¹ See Lewis and Gibson, This Journal, 39, 2554 (1917).

[CONTRIBUTION FROM THE STEELE CHEMICAL LABORATORY, DARTMOUTH COLLEGE]

THE ADSORPTION OF MIXED GASES BY CHARCOAL. I. CARBON DIOXIDE AND NITROUS OXIDE

By Leon B. Richardson and John C. Woodhouse Received September 15, 1923

While the adsorption of single gases by charcoal has been the subject of extensive investigation, similar studies for mixtures of gases have been much less abundant. Bancroft1 states that such work as has been done "indicates that the more readily adsorbed gas displaces the other to some extent, and is adsorbed to a greater relative amount than one would have predicted from experiments on the single gases." The experiments which led to this deduction were, however, largely qualitative; or where quantitative, were carried on at low pressures. Thus Bergter2 investigated the adsorption of nitrogen and oxygen mixtures at very low pressures and Hunter.3 that of a number of easily condensable gases which probably dissolved in one another; Lemon and Blodgett, working at the temperature of liquid air, studied the rate of adsorption of nitrogen-oxygen mixtures; and Miss Homfrav⁵ worked with mixtures of carbon monoxide and nitrogen at -79°. In all these cases, however, the pressures were low and extended through a very limited range; the temperatures were also low; nor was any attempt made to determine the adsorption of the separate gases in the mixture at a number of pressure points. It seemed worth while, therefore, to investigate the total adsorption of gaseous mixtures at 0° through pressures ranging from very low values to a maximum of 3.5 atmospheres, and also to determine at numerous pressure points, by methods of analysis, the adsorption of each gas separately. Carbon dioxide and nitrous oxide were selected as materials for the first study. It is hoped that other pairs of gases will form material for subsequent papers from this Laboratory upon the same general problem.

Materials and Apparatus

Charcoal.—As an adsorbent, steam-activated charcoal⁶ was used. Its density determined in a vacuum in the usual way gave results 1.809 and 1.806. The ash content was 1.87%. The pieces were 8-10 mesh size, and the same sample, weighing 4.5332 g., was used throughout the determinations. The material was highly adsorbent, and took up each time, even after extensive use, nearly the same amount of a given gas.

Gases.—In the selection of gases the following conditions were considered desirable.

(1) The gases should not react upon each other or upon the charcoal. (2) They

¹ Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 16.

² Bergter, Ann. Physik., 37, 472 (1912).

³ Hunter, J. Chem. Soc., 23, 73 (1878).

⁴ Lemon and Blodgett, Phys. Rev., 14, 394 (1919).

⁵ Homfray, Z. physik. Chem., 74, 129 (1910).

⁶ Procured from the Barneby-Chaney Company.

should not, when liquefied, dissolve appreciably in each other. (3) They should be adsorbed to a large extent at 0°. (4) They should be of nearly equal density, to insure quick and easy mixing. These requirements seemed to be met by the selection of carbon dioxide and nitrous oxide. The adsorption of the first has been widely studied; its isotherms have been repeatedly determined. Very little work has been done on the second, but from its physical constants and from the results of Hempel and Vater' it is apparent that its degree of adsorption is comparable to that of carbon dioxide. The only point that caused apprehension was that at the temperature required for out-gassing (425°) the charcoal might be oxidized by the nitrous oxide. Consequently, an analysis of the gas subjected to the action of the charcoal during the out-gassing process was made in each determination of the nitrous oxide isotherm. In no case was the slightest amount of carbon dioxide detected in the gas withdrawn from the cell; nor in the runs of mixed gases was any excess of carbon dioxide over that introduced into the system ever obtained.

The carbon dioxide used was 99.7-99.9% absorbable in potassium hydroxide solution. The nitrous oxide was a commercial product which by analysis was shown to be 98.4-99.1% pure, the sole impurity appearing to be nitrogen. It is difficult to prepare nitrous oxide in sufficient quantities by the ordinary processes of the laboratory of as high purity as this. As the influence of the small quantities of contaminating nitrogen was slight, and as its precise effect on the isotherms could be determined, the gas as procured was deemed sufficiently good for the purpose of these experiments.

Method of Determining Isotherms.—The adsorption isotherms of the mixture were made by running known quantities of the gases into a cell containing the adsorbent. When the maximum pressure was reached the points on the isotherm were determined by withdrawing successive portions of the mixture and analyzing each portion withdrawn. The system was allowed to come to equilibrium and the pressure read after each withdrawal. The apparatus having been carefully calibrated, the volume of the gaseous phase could be determined from the pressure reading, while the volume of each of its components could be obtained by the analysis of the gas withdrawn. The total volume of each gas admitted to the apparatus being known, the volume adsorbed, both total gas and each component, could be determined by difference.

Apparatus.—The apparatus used in the determinations was of the type employed by one of us⁸ in the determinations of the individual isotherms of carbon dioxide and ammonia. It was modified in such details as became necessary through the use of more than one gas, and of their withdrawal for analysis. A diagram of the essential parts is given in Fig. 1. Cell C contains the charcoal, and is connected on one side with the manometer M capable of registering pressures to 3000 mm., and on the other, through the 3-way stopcock A to the 100cc. water-jacketed buret B. To the right, the gas buret is joined through the 3-way stopcock D to the gas supply tubes E and E'. All connecting tubing is of 1 mm. bore, and all connections are made by fusing the glass together.

Carbon dioxide, dried by being passed through a calcium chloride tube and two Friedrichs wash bottles filled with sulfuric acid, was introduced through E. Nitrous oxide, first bubbled through two large Winkler bulbs filled with sulfuric acid, was brought in at E'. This tube also served for the withdrawal of gas and its transfer to the analysis apparatus. If the gas was not required for analysis it was run out through the mercury trap F. By the manipulation of the stopcock A and the mercury-filled leveling bulb L, gas could be pumped into the cell up to high pressures, or out of it through F until a vacuum was obtained. The leveling bulb could be raised by a wire running through a pulley in

⁷ Hempel and Vater, Z. Elektrochem., 18, 724 (1912).

⁹ Richardson, This Journal, 39, 1829 (1917).

the ceiling so that the maximum pressure could be easily secured. After exhausting the cell, gas could be drawn in through E or E', measured under known conditions of pressure and temperature in the buret, and then forced into the cell.

The buret was calibrated in duplicate by weighing its water content. The volume of gas in the manometer at various mercury levels was determined by sealing off the capillary tube connecting the cell with the apparatus and passing in successive volumes of carbon dioxide measured in the buret. Three calibrations were made, the maximum divergence being 0.4%.

The cell was constructed as shown in Fig. 1. Tube a has an internal diameter of 9 mm.; Tube b, 4 mm.; Tube c, 1 mm. The capacity of the cell to the point f was determined thrice with a maximum variation of 0.13%. The volume from e to f was also obtained. The weighed sample of charcoal was introduced through b, and the cell was then sealed off between e and f, care being taken to make a very flat end, thus avoiding any uncertainty of measurement caused by a conical tip. By measurement from e to the end, the fraction of the known volume (e to f) then in the cell could be calculated. The small free space in the capillary above the level f was ascertained by calibration of

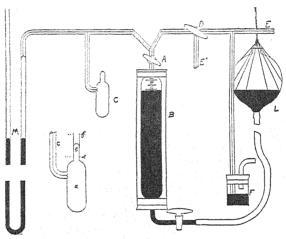


Fig. 1

other pieces of the same tubing. The total volume of the cell thus obtained was 8.45 cc. The volume of the charcoal in the cell, determined from its weight and density, was 2.51 cc. The free space in the cell was thus 5.94 cc. The tubing of the apparatus was cut off at a measured distance above the point at which it was sealed during the manometer calibration, and the volume thus removed was subtracted from that calibration. The volume of capillary tubing from point e to the point at which the fused joint was made was also calculated and added to the cell volume. The volume of the gas in the cell at various pressures (corrected in accordance with the data of Regnault) and at a temperature of 0° was added to the volume of gas in the manometer at the same pressures and at the temperature of the manometer calibration ($20^{\circ} = 1^{\circ}$). These total volume results were plotted, and from the curve obtained the volume of the gaseous phase could be read at any pressure registered by the manometer.

As all determinations were made at 0°, temperature regulation was effected by a bath of finely divided ice and water. The variation was less than 0.1°. The thermometers used in determining the temperatures of the bath, the manometer, and the buret were checked against one another and against a standard thermometer graduated to 0.1°.

Analysis

The successful prosecution of the work required an accurate method for the analysis of mixtures of carbon dioxide and nitrous oxide. The ordinary methods, namely, absorption of carbon dioxide in potassium hydroxide, and the explosion of nitrous oxide after mixture with a measured volume of hydrogen, are accurate enough for each gas separately but require modification when the gases are mixed. The difficulty lies in the solubility of nitrous oxide in the potassium hydroxide, which is sufficiently great under ordinary circumstances to vitiate the process. It was necessary, therefore, to determine just how much nitrous oxide is dissolved in solutions of potassium hydroxide of various concentrations. It was found that although solutions of the alkali of concentrations usual in gas analysis (30-40%) do dissolve sufficient amounts of nitrous oxide to make the separation inaccurate, a 55% solution, after the first exposure of nitrous oxide to it, takes up only inappreciable amounts of the gas. Fresh solution of this concentration placed in contact with 100 cc. of nitrous oxide for three hours dissolved only 1.4 cc.; a much smaller amount than is taken up by alkali solutions of lower concentrations. After this exposure of the fresh potassium hydroxide solution, nitrous oxide was again placed over the solution for the period of 10 minutes or so customary in gas analysis, and also for longer periods, both alone and mixed in various proportions with carbon dioxide. In no case was any nitrous oxide given off from the liquid or any more dissolved by it. This decrease of solubility is in accord with the results of Geffcken⁹ although his work was not carried to such high concentrations of alkali. Extrapolation of his figures gives solubilities of nitrous oxide in potassium hydroxide solutions very close to those here obtained.

Attention should be called to two precautions necessary in the ignition of mixtures of nitrous oxide and hydrogen which are not mentioned in the texts on gas analysis. Incomplete mixing of the two gases not infrequently causes feeble explosions. The gases should be passed from the buret to the pipet and back several times. Even more important is the necessity for the presence of a small amount of water (0.5–1 cc.) in the explosion pipet. Again and again, in cases in which it had been found impossible to initiate an explosion when the gases were dry, the spark became thoroughly effective after the addition of this small quantity of water. Consequently, assurance of the presence of water was finally made a matter of routine practice in the analysis.

Variations in the volume of gaseous mixtures from the sum of the volumes of the component gases before mixing may also have an effect upon the results. Fuchs¹⁰ presents data covering various mixtures; among others,

⁹ Geffcken, Z. physik. Chem., 42, 257 (1904).

¹⁰ Fuchs, ibid., 92, 641 (1918).

carbon dioxide and nitrous oxide. His results seem to show that a 50–50 mixture of these gases occupies a volume 1.42% greater than the sum of the volumes of the individual gases. Investigations of our own showed that the expansion, in this case at least, is approximately that indicated by Fuchs. From his data, therefore, a graph was drawn which indicated what this variation should be for all proportions of mixtures of the gases in question, and what corrections should be made in each analysis. It should be said, however, that this correction exercises so slight an influence upon the final result as to make its effect almost negligible.

Experimental Procedure

The amount of gas adsorbed by charcoal is dependent upon many seemingly unimportant factors. Slight variations in conditions produce relatively great variations in results. If values are to be duplicated, the process must be standardized and, when thus standardized, accurately followed. This done, as described below, no difficulty was found in obtaining close duplicates of the isotherms, both of single gases and of each mixture with which experiments were made.

To prepare the charcoal for the adsorption, the cell was heated to 425° by an electric furnace, gas being pumped out at frequent intervals as it escaped. In the course of four hours the pressure was reduced to not more than 1 mm., even at the high temperature. The cell was then cooled slowly (20 minutes) to 0°, and allowed to remain for 10 minutes at this point before any gas was run in. In the meantime gas, carbon dioxide or nitrous oxide, as might be desired, was being passed in through E or E' and out through F, so that residual gas might be removed from that part of the apparatus. The two gases were then admitted to the buret in such proportions as might be desired, and mixed by raising and lowering L several times. The amounts run in were such that their total volume would equal the capacity of the buret, and in the proportions which were desired in the final mixture. The contents of the buret as a whole were then admitted to the cell. It was found especially important for the duplication of results that the volume of each portion admitted should be uniform. When equilibrium was attained, as shown by the constancy of the level in the manometer, a fresh portion, which in the meantime had been prepared in the buret, was run in. This process was continued until no more gas could be forced in at the maximum pressure attainable by the apparatus. The capillary from A to the cell was then sealed with a thread of mercury to prevent any possible chance of leakage, and the gas left at 0° overnight.

Inasmuch as the gaseous phase was to be analyzed and the composition of the adsorbed phase determined thereby, measurement of the adsorption isotherms had to be made during withdrawal of the gas. Such isotherms

are subject to a lag of gas leaving charcoal as compared with those determined from data obtained by measuring equilibrium pressures of gases "going in." This lag has been previously observed and is confirmed in this work. The results here obtained, however, are comparable with each other, for the lag is a relatively constant factor in them all. The question of lag will be discussed in detail in the theoretical section following.

The withdrawal of gas was made in 50cc. fractions. After measurement in the buret the gas was driven through E' to a Hempel gas buret and analyzed, correction being made for the expansion due to the mixing of gases and to the tension of aqueous vapor in the pipets. This withdrawal was continued in successive portions until the pressure was not more than 75 mm. As numerous points low in the curve were not especially inportant in this work, and as the amounts of gas which could be withdrawn by evacuation alone from this point on were extremely small, the cell was heated and all the rest of the gas was driven out. The final result gave about 14 readings for each isotherm.

The total volume of gas withdrawn agreed very closely with that admitted, the average variation being about 2 cc. in 750 cc. The same can be said of the component gases measured "going in" and analyzed "coming out."

The carbon dioxide was to all intents pure, and no difficulty was experienced in accounting for all the gas introduced; the deviations in the nitrous oxide were almost exactly equal to the nitrogen contained in the original gas (1-1.5%). Practically all of this impurity was found in the first fraction withdrawn.

As a result of this standardization of the manipulation, a surprisingly close duplication of results was obtained, both with the gases unmixed and with each of the mixtures studied, a condition not always reached in studies of adsorption by charcoal. This duplication was true of the total amount adsorbed, of the general shape of the curves, and of the amounts of the individual gases adsorbed from mixtures and their adsorption curves. In the case of each curve, duplicates were obtained in which the variation was not more than 0.5%, a smaller difference than could be shown in any plotting of the curve on an ordinary scale.

As the nitrous oxide was slightly impure, an individual run was made to see whether increased purity changed the shape of the isotherm. It has been stated above that practically all of the impurity remained unadsorbed and was removed in the first portion of the gas withdrawn, the succeeding portions analyzing over 99.7%. For this reason an isotherm run was started in the usual way, with 99% nitrous oxide from the cylinder. When the maximum pressure was reached, the system was left for four hours; then 100 cc. of gas was withdrawn and replaced by fresh nitrous oxide, thus raising the purity of all the gas in the system to 99.8%. After

the mixture had stood overnight the isotherm was determined in the usual manner. Its deviation from the isotherms previously produced without this special care was negligible. The two were identical below 2200 mm, and the variation at the highest pressure was only 1%.

Experimental Data

Table I gives the essential data for the individual adsorptions of carbon dioxide and nitrous oxide unmixed. The figures show the volume of each gas in cc. adsorbed per gram of charcoal at the pressures stated.

Table I Adsorption of Each Gas Separately

CO		N_2	0
Pressure Mm.	Gas in system, Meas. in, 677.1 cc.; meas. out, 672.7 cc. Adsorb. Cc.	Pressure Mm.	In, 671.8 ec.; out, 673.0 ec. Adsorb. Ce.
90.4	24.6	61.5	26.0
176.2	34.0	110.4	35.8
271.9	45.7	178.8	45.7
399.4	55.3	262.6	55.1
552.6	64.7	369.2	64.4
734.0	73.8	504.3	73.5
950.2	82.4	674.4	82.7
1207.1	91.6	881.4	90.5
1478.2	97.9	1138.4	99.3
1829.1	104.1	1447.8	106.1
2155.9	110.1	1666.8	109.9
2506.0	114.9	2041.5	113.3
2864.8	119.1	2396.0	115.8
		2842.3	118.6

These results are given in graphical form in Fig. 2.

Table II

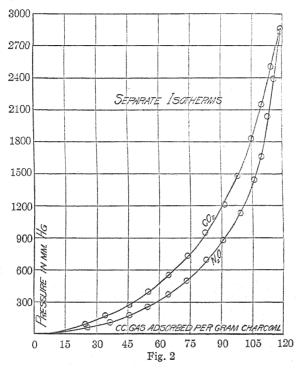
Adsorption of a Mixture of 49.2 Per Cent. of Carbon Dioxide and

PTION OF A MIXTURE OF 49.2 PER CENT. OF CARBON DIOXIDE AND
50.8 PER CENT. OF NITROUS OXIDE

Gas in 672.3 cc. Gas out, 670.8 cc. Temperature 0°

	,	0.2.0	~~.		out,	0.0.0		T CIMPO	xacut	.0
Pressure Mm.			Total	ads.		co)2 ads.	_	:	N2O ads.
72.8			26	0.6			8.6			17.4
127.6			35	.1			12.7			22.4
206.7			44	.9			17.4			27.4
316.8			54	.8			22.5			32.3
420.4			62	.4			26.5			35.9
572.7			72	0.3			31.7			40.3
773.1			- 80	.5			36.4			44.1
1010.4			89	.1			41.1			48.0
1298.3			97	.1			45.5			51.6
1625.6			103	.6			49.1			54.5
1983.2			109	.3			52.3			57.0
2366.1			113	.6			54.7			58.9
2870.5			117	.5			57.3			60.2

Three mixtures of the gases were investigated. These contained approximately 50% CO₂-50% N₂O, 75% CO₂-25% N₂O, and 25% CO₂-75%



 N_2O , respectively. The results are given in Tables II, III and IV. The first column records the pressures in millimeters; the second, the total vol-

Table III

Adsorption of a Mixture of 73.9 Per cent. of Carbon Dioxide and 26.3 Per cent.

of Nitrous Oxide

Gas in, 666.7 cc. Gas out, 665.8 cc. Temperature 0° Pressure CO2 ads. N2O ads. Total ads. Mm. 13.0 9.222.2 58.3 11.8 31.1 19.3 113.9 14.4 40.6 26.2187.8 16.8 50.2 33.4286.519.0 59.8 40.8 416.1 47.8 20.968.8 567.6 55.0 22.977.9 748.0 24.6 86.4 61.8984.226.268.0 94.21251.3 73.727.7 101.41556.229.0 78.4 1899.0 107.482.1 30.0 112.1 2263.8 87.1 9.08118.0 2781.0

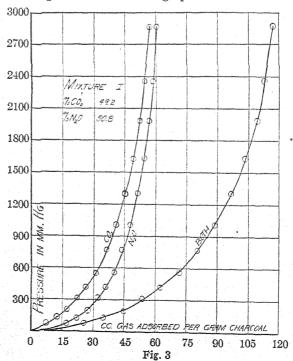
ume of the mixture adsorbed; the third, the volume of carbon dioxide adsorbed; and the fourth, the volume of nitrous oxide adsorbed, in each case per gram of charcoal. Col. 2 gives results obtained by measurement of the residual gas; Cols. 3 and 4 from the analytical figures in each case (not by difference).

Table IV

Adsorption of a Mixture of 23.4 Per cent. of Carbon Dioxide and 76.6 Per cent. of Nitrous Oxide

Gas in,	674.2 cc. Gas out,	675.6 cc. Temperature,	0°
Pressure Mm.	Total ads.	CO2 ads.	N2O ads.
77.3	28.9	3.9	25.0
137.4	38.9	5.8	33.1
220.1	48.9	8.1	40.8
322.6	58.3	10.4	47.9
431.0	66.2	12.2	54.0
607.4	75.3	14.7	60.6
1011.6	92.4	19.7	72.7
1287.3	99.5	21.9	77.6
1610.4	106.0	23.7	82.3
1988.0	111.4	25.3	86.1
2404.0	115.4	26.7	88.7
2858.0	118.9	27.8	91.1

Figs. 3, 4 and 5 give these results in graphical form.

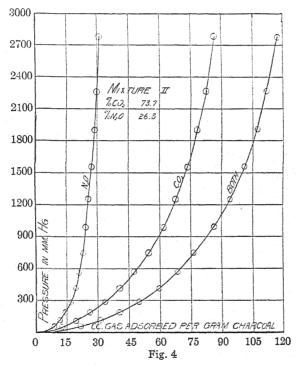


Discussion

From the data given above it seems possible to deduce the total amount of any mixture of carbon dioxide and nitrous oxide adsorbed by charcoal, if the isotherms of the independent adsorption of the individual gases are known. The formula

$$V_{\text{mixt}} = \frac{V_{\text{N2O}} a_1 + V_{\text{CO2}} a_2}{100}$$

in which $V_{\text{N}_2\text{O}}$ and V_{CO_2} represent the volumes of those gases separately adsorbed at the total pressure of the mixture, and a_1 and a_2 stand for the



percentages of the respective gases in the mixture, holds within reasonable limits, as shown in Table V.

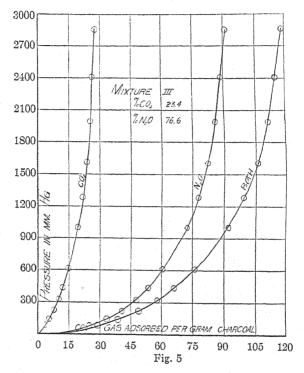
Table V

Volume of Mixture Adsorbed, Calculated from Separate Adsorption Curves,

Compared with Values Experimentally Determined

Pressure Mm.	"50–50 r Calc.	nixt." Obt.	"75-25 Calc.	mixt.'' Obt.	"25-75 r Calc.	nixt." Obt.
2800	118.3	117.1	118.4	118.4	118.3	118.5
1600	104.2	102.4	102.2	102.3	106.4	105.8
1000	89.7	88.7	87.3	87.0	92.3	91.9
600	73.4	73.2	70.6	70.2	76.5	75.1
200	44.1	43.7	41.7	41.4	46.7	47.1

When we consider that under the best of conditions the amount of gas adsorbed by a given specimen of charcoal varies several cubic centimeters in duplicate determinations, this agreement seems remarkably close. It should be said, however, that the relative nearness to each other of the



isotherms of the two gases under consideration is particularly favorable to the application of the above formula. It might not work so well with other pairs of gases.

Table VI RATIO OF ADSORPTION: N_2O/CO_2

		TYPOONE TION . TA	20/002	
Pressure Mm.	Ind. ads.	"50–50"	"75–25"	"25-75"
2800	1.00	1.02	1.00	1.00
2400	1.018	1.05	1.02	1.02
2000	1.03	1.06	1.03	1.05
1600	1.084	1.07	1.05	1.06
1400	1.09	1.08	1.06	1.08
1200	1.102	1.10	1.08	1.10
1000	1.114	1.12	1.11	1.14
800	1.146	1.17	1.15	1.19
600	1.173	1.23	1.20	1.26
400	1.204	1.32	1.34	1.35
200	1.256	1.54	1.53	1.56

On the other hand, there seems to be no possibility of calculating the volume of each of the component gases adsorbed in the charcoal from the total volume of the gaseous mixture. In other words the ratio of the amounts of the two gases adsorbed varies with the pressure, whether we are dealing with them as separately in contact with the charcoal, or whether they are mixed. This fact is shown by the data given in Table VI. Col. 1 gives the pressure, Col. 2 the ratio N_2O/CO_2 in independent adsorption, Cols. 3, 4 and 5 similar ratios (the volume of each gas being multiplied by the percentage of the other in the mixture) for the three mixtures studied. It will be seen that at the lower pressures there is a continually increasing proportion of nitrous oxide adsorbed.

This point has been touched upon, in connection with other gases, by a number of other investigators. Bergter, working at pressures of not over 10 mm. with mixtures of nitrogen and oxygen, concluded that while the relationship in which the two gases are adsorbed depends very considerably upon the pressure, under conditions with which he worked oxygen is adsorbed 30 to 40 times as much as nitrogen. He also came to the curious decision that the presence of adsorbed nitrogen more than doubles the capacity of charcoal to take up oxygen. Lemon and Blodgett, working with the same gases at low pressures and at the temperature of liquid air, believe, on the contrary, that there is a nearly linear relation between the logarithm of the equilibrium pressure and the percentage of oxygen in the mixture; and that gases are not adsorbed "independently"—that the presence of one gas reduces the capacity of the charcoal to take up another. Miss Homfray, as a result of a series of single determinations of mixtures of carbon monoxide and nitrogen at pressures up to one atmosphere and at -79°, comes to the conclusion that the relative volumes of these gases adsorbed under the conditions stated is constant within an error of 2%. She made, however, no determination of a complete isotherm for any mixture, nor did she analyze the unadsorbed gases, but based her deductions on the fact that the total volume adsorbed was what it should be to satisfy a formula similar to that given above. Her conclusion, therefore, while probably valid for the total adsorption of the mixture, cannot be considered as indicating anything quantitatively definite as to the adsorption of the individual gases of the mixture.

Molecular Volumes and Adsorption

Recently suggestions have been made that a proportionality exists between degree of adsorption and the molecular volumes of the adsorbed gases. Thus Wilson, 11 using the data of Lemon and Blodgett, calls attention to the fact that in their work the ratio of moles of nitrogen adsorbed

11 Wilson, Phys. Rev., 16, 8 (1920).

to moles of oxygen is very nearly 1 to 1.3, which is the inverse ratio to their molecular volumes. Lamb and Coolidge, ¹² in researches on the adsorption of the vapors of carbon tetrachloride, ether, methyl alcohol, etc., find that a similar relationship holds. They further point out that the figures of Titoff¹³ on the adsorption of ammonia and carbon dioxide (as single gases) permit a similar conclusion. It is to be noted, however, that the pressure points at which this last relation was found to hold were selected, apparently by chance, at 20 mm.

It is obvious from an inspection of the figures in Table VI that in our work, either with single gases or with mixtures, such a relationship holds only within a limited pressure range. For the single gases the ratio varies from 1 at 2800 mm. to 1.256 at 200 mm. For the mixtures there is a similar but greater variation, reaching a maximum of 1.56 at 200 mm. The ratio of the molecular volumes of carbon dioxide and nitrous oxide is 1 to 1.025. ¹⁴ It may then be stated that, within the experimental error, the gases herein studied are adsorbed inversely as their molecular volumes at pressures ranging from 1800–2800 mm. only; and that, below this, the lower the pressure, so far as the results of this investigation can be brought to bear upon the problem, the greater the divergence from this rule. It should be noted, however, that the apparatus used in this investigation was not adapted for the determination of equilibrium points at very low pressures, and such values are not given.

As all comparisons between adsorption and molecular volumes have been made at low pressures, except those discussed in this paper, it is of interest to apply the method to previously obtained isotherms of gases over as wide a pressure range as possible, and thereby to determine whether these ratios vary as they seem to do in the present work. The comparison must, of course, be made upon the basis of data obtained from the isotherms of single gases, as mixtures have not been studied. Ammonia and carbon dioxide have been investigated through a wider pressure range than other gases: at pressures up to one atmosphere by Titoff, and at higher points by one of us.

Table VII

Ratio of Adsorption: CO₂/NH₂, at Various Pressures

Pressure Mm.	Ratio Richardson	Titoff Ratio	Pressure Mm.	Ratio Richardson	Ratio Titoff
1600	2.00		200	2.28	2.28
1200	2.07		100	• •	2.30
800	2.15	2.05	50	2.10	2.09
600	2.21	2.12	25		1.80
400	2.28	2.26	2	• •	1.75

¹² Lamb and Coolidge, This Journal, 42, 1146 (1920).

¹⁸ Titoff, Z. physik. Chem., 74, 641 (1910).

¹⁴ Cailletet and Mathias, Compt. rend., 102, 1202 (1886).

The results of the comparison are given in Table VII; temperature 0°. The ratio of the molecular volumes is 1.81. Apparently, then, at 0° for very low pressures with these gases, the inverse proportionality of the adsorption to the molecular volume holds; at higher pressures the deviation increases, reaching a maximum at 100 mm. From that point, as far as these results go, it decreases. Extrapolation of Richardson's results indicate that at a pressure of 3.5–4 atmospheres the adsorption of carbon dioxide and ammonia again approaches a ratio which is inversely proportional to the molecular volumes, as it was found to be in the case of carbon dioxide and nitrous oxide in the present work.

Replaceability of One Gas by Another

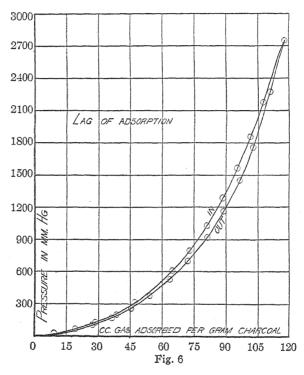
In all the experiments described above, the gases were mixed before being admitted to the charcoal. It seemed worth while to compare the result thus obtained with that gained by adding one gas (nitrous oxide) to the other, already adsorbed by the charcoal. After a certain time interval the unadsorbed gas was withdrawn and analyzed, and the composition of the gaseous phase was determined. This was compared with the composition of the gaseous phase obtained from a mixture of the same composition, admitted to the charcoal subsequent to mixing, and showing approximately the same pressure (data obtained in the course of the work previously described). The experiment was then repeated at longer time intervals until the general course of the reaction could be determined. The findings are given in percentages of unadsorbed gas: the upper value (gases mixed before adsorption) being, of course, the limit to which the others should approach.

Pressure Mm.	Time Hrs.	%N2O	%C02
1403.5		21.1	78.9
1488.9	3	47.3	52.7
1428.0	18	35.6	64.4
1400.8	39	33.9	66.1

These figures indicate that although replacement goes on rapidly at first, it proceeds at a much slower rate when about half the gas that one would expect to be replaced has been thus driven out. The speed of the action then becomes so small that it is doubtful whether an equilibrium close to that obtained with the previously mixed gases would ever be reached.

Lag

As all measurements in these determinations were made on gas withdrawn from the charcoal, they are subject to the lag of gas thus leaving, compared with the amounts entering at the same pressure. A study of the exact effect of this lag seemed desirable. It was found to be sufficiently uniform, both with the separate gases and with the mixtures, so that the results as obtained could be considered as strictly comparable. The two isotherms of carbon dioxide "going in" and "coming out" are given in Fig. 6. It will be seen that the lag reaches a maximum of about 5% at pressures from 1000 to 1600 mm., and decreases continuously toward either pressure extreme.



Summary

- 1. The adsorption isotherms of carbon dioxide and nitrous oxide independently, and in mixtures of the approximate proportions 50% CO₂–50% N₂O, 75% CO₂–25% N₂O, and 25% CO₂–75% N₂O have been determined at 0°, and through pressure ranges up to 2800 mm.
- 2. At each reference point of the three isotherms of the mixtures the amounts of the carbon dioxide and nitrous oxide adsorbed have been determined by analysis.
- 3. The total amount of the mixture adsorbed can be calculated from the independent adsorption isotherms of the individual gases.
- 4. The ratio of the degree of adsorption of the two gases varies with the pressure. Only at the highest pressure is it found to be in inverse ratio to the molecular volumes of the adsorbed substances in the liquid form.

Calculations from other work make it probable that a similar ratio holds at very low pressures.

- 5. It was shown that a gas admitted to another already adsorbed by charcoal replaces it rapidly at first, then with increasing slowness, and that replacement never goes so far as to give an amount of the second gas adsorbed equal to that which would be adsorbed from a mixture of the same composition mixed before being admitted to the charcoal.
- 6. A considerable lag in the adsorption isotherm obtained from carbon dioxide leaving charcoal compared with that obtained when the gas was entering it was detected; the lag amounted at its maximum to 5%.
- 7. The problem of the analysis of mixtures of carbon dioxide and nitrous oxide was satisfactorily worked out.

HANOVER, NEW HAMPSHIRE

[Contribution from the Gates Chemical Laboratory of the California Institute of Technology, No. 34]

THE SOLUBILITY OF POTASSIUM PERCHLORATE IN SALT SOLUTIONS AND THE CORRESPONDING ACTIVITY RELATIONS

By Richard M. Bozorth Received September 22, 1923

Introduction

Activity values may be derived, as is well known, from the solubilities of salts in solutions of other salts through the following considerations. In any solution saturated at a definite temperature with a uni-univalent salt such as AB the product of the activities $a_{\rm A} \times a_{\rm B}$ of the ion constituents A and B has a constant value whatever other salts may be in the solution. Expressing the concentration of the ion constituents by c with appropriate subscripts and putting the activity coefficient $\alpha = a/c$, we may write for any such solution

$$c_A \alpha_A c_B \alpha_B = a \text{ constant, or } \frac{\alpha_A \alpha_B}{\alpha_{A0} \alpha_{B0}} = \frac{c_{A0} c_{B0}}{c_A c_B}$$

where the subscripts zero refer to the solution in pure water. Hence from solubility data the change can be determined of the activity-coefficient product with the nature and concentration of an added salt, or with the total concentration of the solution.

The purpose of the work described in this paper was to determine to what extent the activity-coefficient product for potassium perchlorate is dependent on the nature of the ions added to the solution. The ions for which the effect has been determined are: K⁺, Na⁺, Ba⁺⁺, Cl⁻, NO₃⁻, ClO₄⁻, SO₄⁻⁻, the added salts producing these ions being KCl, KNO₃, K₂SO₄, NaCl, NaNO₃, NaClO₄, Na₂SO₄, BaCl₂, and Ba(NO₃)₂. The total

concentrations of the saturated solutions were carried as high as 0.7–0.8 N. This work was carried out at the suggestion and with the advice of Professor A. A. Noyes, to whom I wish to express my appreciation. It was assisted financially by a grant made to him from the Carnegie Institution of Washington.

Method of Determining the Solubility

Solubilities were determined at 25°, following the method previously used by Noyes and Boggs.¹ Potassium perchlorate was recrystallized until no test for chloride ion or chlorate ion was obtained, one recrystallization being usually sufficient. Other salts were of good commercial "analyzed" quality once recrystallized, with the result that in salts other than chlorides no chloride could be detected. The salt contents of the solutions were determined by evaporating a weighed portion on a steam-bath and drying the residue to constant weight at 200°. After the solutions were saturated with potassium perchlorate, they were filtered within the thermostat, and the total salt in them determined by evaporating and weighing. Knowing the amount of salt associated with a given amount of water in each salt solution, the amount of perchlorate in the saturated solution was determined by the difference.

Saturation was approached from both the under- and over-saturated sides in the case of about half the solutions; but as no systematic difference could in any case be detected, the other determinations were made without regarding the method employed.

The Solubility Data

The results of the solubility determinations are given in Table I. The salt contents are all expressed in equivalents of salt per 1000 g. of water. The values at the foot of each section of the table are means of the (usually) four separately determined values above them.

TABLE I

THE SO	LUBILITY	of Por	ASSIUM	PERCHLOR.	ATE IN	Solutions	of Other	R SALTS	ar 25°
NaCi	KC104	KCI	KC1O ₄	NaClO ₄	KC104	$NaNO_3$	KClO ₄	Na ₂ SO ₄	KC104
.1006	.1567	.0985	.1138	.1027	.1117	.1008	.1610	.1047	.1633
.1007	.1566	.0983	.1135	.1026	.1123	.1008	.1610	.1047	.1633
.1007	.1568	.0980	.1135	.1025	.1123	.1007	.1611	.1047	.1634
.1008	.1568	.0984	.1136	• • •	.1122	.1008	.1612	.1048	.1626
.1007	.1567	.0983	.1136	.1026	.1122	.1008	.1611	.1047	.1633
.2995	.1659	.2993	.0758	.3091	.0751	.3141	.1789	.3210	.1801
.2991	. 1659	.2995	.0757	.3088	.0752	.3138	.1791	.3211	.1802
.2992	.1657	.2995	.0751	.3090		.3140	.1780	.3209	.1800
.2991		.2995				.3138	.1790	.3210	.1799
.2994	.1558	.2994	.0757	.3090	.0752	.3139	.1790	.3210	.1800

¹ Noyes and Boggs, This Journal, 33, 1650 (1911).

SOLUBILITY OF P	OTASSIUM	CHLORATE
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.5906	.1732	.6089	.0534	.6273	.0532	.6218	. 1995	.6610	.1954
. 5903	.1732	.6087	.0536	.6273	.0535	.6221	.1993	.6610	.1959
. 5901	.1732	.6089	.0529				.1994	.6610	
.5901	.1730	.6090	.0535				.1992	.6610	
. 5903	.1732	.6089	.0535	.6273	. 0533	.6220	.1994	.6610	.1957
KNO3	KClO ₄		K ₂ SO ₄	KC104	BaCl ₂	KC	104	Ba (NO ₅) ₂	KC104
.0971	.1174				.099	1 .15	69	.0988	.1612
.0971	.1175				.099	1 .15	69	.0991	.1592
.0971	.1173								.1612
	.1175			• • •					
.0971	.1174		$.0998^{a}$	$.1194^{a}$.099	1 .15	69	.0990	.1605
.2955	.0844		.3024	.0857	.297	5 .16	37	.3019	.1756
.2953	.0847		.3026	.0857	.297	1 .16	38	.3016	.1726
.2953	.0848		.3025	.0855	.297	4		3021	.1760
	.0844							.3018	
.2954	.0846		.3025	. 0857	.297	4 .16	38	.3019	.1747
.6686	.0641		.6011	.0641	. 599	6 .16	92	.6074	.1896
.6687	.0654		.6004	.0644	.599	5 .16	94	.6077	.1907
.6686	.0639		.6005	.0649		·. • •		.6076	
	.0636		.6012				•	.6073	•••
.6686	.0642		.6008	.0644	.599	5 .16	93	.6075	.1902

 $[^]a$ Derived from the results of Noyes and Boggs, Ref. 1.

The Values of the Activity Coefficient

Table II contains the mean values of the solubility, transferred from Table I, the salt content being here expressed in milli-equivalents per 1000 g.

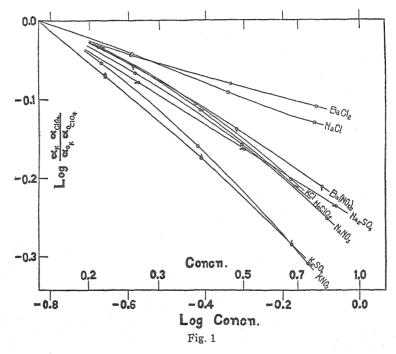
TABLE II THE VALUES OF THE ACTIVITY-COEFFICIENT PRODUCT

Adde Nature	d salt	Actcoef. Solubility product		Added Nature	salt Content	Solubility	Actcoef. product
		- ·	•			-	-
None	0	149.1	1.000	None	0	149.1	1.000
KC1	98.3	113.6	0.923	K_2SO_4	99.8	119.4	0.849
	299.4	75.7	.783		302.5	85.7	.668
	608.9	53.5	.627		600.8	64.4	.519
KNO_3	97.1	117.4	.883	Na_2SO_4	104.7	163.3	.834
	295.4	84.6	.691		321.0	180.0	.686
	668.6	64.2	.490		661.0	195.7	.580
NaClO ₄	102.6	112.2	.922	BaCl ₂	99.1	156.9	.903
	309.0	75.2	.769		297.4	163.8	.829
	627.3	53.3	.613		599.5	169.3	.776
NaCl	100.7	156.7	.905	$Ba(NO_3)_2$	99.0	160.5	.875
	299.4	155.8	.809		301.9	174.7	.728
	590.3	173.2	.741		607.5	190.2	614
NaNO ₃	100.8	161.1	.857				
	313.9	179.0	.694				
网络克勒马斯 医电子形成型				to the contract of the contrac			

of water. The last column of each half of the table contains the activity-coefficient product, $\alpha_{\rm A}\alpha_{\rm B}/\alpha_{\rm A_0}\alpha_{\rm B_0}$, calculated from the inverse solubility-product ratio, $c_{\rm A_0}c_{\rm B_0}/c_{\rm A}c_{\rm B}$, in accordance with the principles described in the Introduction of this article.

Discussion of the Results

The logarithm of the activity-coefficient product is plotted against the logarithm of the total salt content in Fig. 1. The striking fact shown by the graphs is that each added ion has a specific effect independent of the other ion with which it is associated. Thus potassium ion has a much



greater effect than sodium or barium ion in reducing the activity-coefficient product of potassium perchlorate, and the sodium ion has an only slightly greater effect than barium ion, these statements being true whether these ions are present with chloride, nitrate, or sulfate ion (in the cases of potassium and sodium ion). Similarly, chloride ion always exerts a much smaller effect than nitrate or sulfate ion, while the last two ions have nearly the same influence.

These effects are clearly brought out also by the values shown in Table III of the activity-coefficient product interpolated for a total concentration of $0.5\ N$. The differences in the product caused by replacing one ion by another are seen to have a definite value no matter what ion of opposite

sign is present with the two ions to be compared; for example, the difference in the activity-coefficient product caused by replacing potassium by sodium is about 0.09 whether the potassium and sodium are associated with chloride, nitrate or sulfate.

Table III

Values of the Activity-Coefficient Product at a Total Concentration of 0.5

				Norma	L,			
Salt added	Activity product	Differ- ence	Salt added	Activity product	Differ- ence	Salt added	Activity product	Differ- ence
KC1	0.705		KNO_3	0.600		K_2SO_4	0.597	
		0.093	0.090				0.089	
NaC1	.798		NaNO:	. 690		Na_2SO_4	.686	
		.023			.027			
$BaCl_2$.821		Ba(NO	$(3)_2$. 717				
KC1	.705	;	NaCl	.798		$BaCl_2$.821	
		.105			.108			. 104
KNO_3	.600	l garage	NaNO:	.690		Ba(NO	$_3)_2$.717	
		.003			.004			
K_2SO_4	. 597		Na_2SO_4	.686				

These results show that the effects of the different ions are specific and additive at the fairly large concentrations $(0.25\text{--}0.75\ N)$ here prevailing. These specific effects are so marked as to hide any influence of the valence of the added ion; thus at the same normality barium ion has not far from the same effect as sodium ion, but a much less effect than potassium ion, and sulfate ion has nearly the same effect as nitrate ion, but a much greater effect than chloride ion.

Summary

The solubilities of potassium perchlorate have been determined in 0.1, 0.3, and 0.6 N solutions of the salts KCl, KNO₃, K₂SO₄, NaCl, NaNO₃, NaClO₄, Na₂SO₄, BaCl₂ and Ba(NO₃)₂. The individual effects of the separate ions on the activity-coefficient product of the potassium and chlorate ions have been compared, and at the concentrations involved (0.25–0.75 N) have been found to be markedly specific and additive.

Pasadena, California

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

SURFACE ENERGY OF SEVERAL SALTS

By Merle L. Dundon¹ Received September 28, 1923

Introduction.—In a previous article² the method of calculating surface energy from the increased solubility of fine particles was considered, and a value for the surface energy of gypsum calculated from new data. In the present work an attempt has been made to measure the change in solubility due to change in size of particles for several other substances. The best

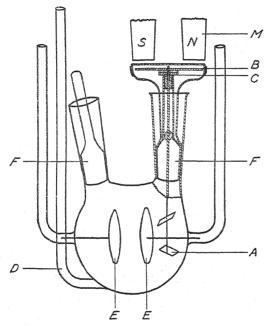


Fig. 1.—Conductivity cell

opportunity for such an investigation occurs with suby stances of small solubility. in which case equilibrium comes about with such slowness that it can be followed by frequent conductivity measurements. Such solubility equilibria must, however, be easily obtained, and continued hydrolysis other decomposition in solution must not occur. With many of the substances considered, such as lead sulfate, mercurous chloride magnesium fluoride, some interfering factor of this sort soon developed, which made it impossible to obtain data of use in this study. those substances which gave

positive results and which are mentioned in this paper, lead fluoride, because of its many favorable properties, was investigated most extensively.

Experimental Method.—Fine powders have been obtained by hand-grinding in an agate mortar, with a mechanically operated mortar and pestle, or with a steel ball mill. Ordinarily, the powder was used directly, and the size of the smallest particles present in large numbers was the value recorded. Attempts were made to sort the particles into different sizes and to calculate the sizes by settling in water or alcohol, making use of Stokes' law. This method failed to yield satisfactory results because of the coalescence of the settling particles into clumps and also, no doubt, because of the adsorption effect at the surface of the small particles.³ In the case of lead fluoride, how-

¹ National Research Fellow, 1922-1923.

² Dundon and Mack, This Journal, 45, 2479 (1923).

³ Williams, Trans. Faraday Soc., 18, 53 (1922).

ever, an air elutriation method was devised, of such a sort that the powder was carried upward through a long glass tower, and very uniformly sized particles, 0.3μ , were obtained, with no particles larger than 0.5μ . Consequently, a good deal of confidence may be placed in the results for lead fluoride.

Measurement of the size of particles was made with a calibrated scale in the eyepiece of a microscope having a magnification of 1800 diameters. Several conductivity cells were used, including the Kohlrausch type, some large flasks with suspended electrodes, and one cell especially designed for this work. This cell is shown in Fig. 1. The platinum paddle-wheel stirrer A can be operated by a magnet M outside the cell. The stirrer shaft of platinum was set into a brass plug at the top and had a drop of glass fused around it lower down to keep it in position. The steel bar B was fastened to the brass plug with a small screw which passed through the washers C. All metal parts other than the platinum were gold-plated. The glass cap above the bar is held in position by a rubber band. F is the ground-glass stopper.

The data for calculating concentrations from conductivity values, such as temperature coefficients, equivalent conductivities, etc., have been obtained in most cases from the work of Kohlrausch. A water correction has been applied to all conductivity values given.

Lead Fluoride

No crystallographic data concerning lead fluoride could be found in the literature and no crystals larger than a few microns were made. However, it was determined that they belong to the orthorhombic system and have an average refractive index of 1.83 and a hardness of about 2.

Hydrolysis of the Solution.—Saturated lead fluoride solutions are distinctly acid, having a Sörensen value of about 1, and the acidity changes very little over a considerable range of dilution. Kohlrausch⁵ found that in the variation of equivalent conductivity with dilution at 18° hydrolysis was not indicated, and his results on this point have been widely quoted. It was found in this investigation at 25° that, although a given solution remained constant, considerable hydrolysis took place on dilution, giving a value for the equivalent conductivity at infinite dilution which is much too high.

Calculation of Concentrations.—A carefully prepared saturated solution had a conductivity of 513×10^{-6} mhos, and gravimetric analysis showed the equivalent concentration to be 0.00555. Experimental data were then obtained from which a curve of equivalent conductivity against the cube root of the concentration was plotted. From this a second curve was plotted giving equivalent concentrations directly in terms of specific conductivity. Several gravimetric analyses of supersaturated solution prepared from fine powder checked this curve almost exactly.

Method of Obtaining Equilibrium.—A saturated solution was pipetted into the cell from a stock solution, powder added and the cell shaken

⁴ Thanks are due to Professor W. J. McCaughey of the Department of Mineralogy, Ohio State University, for assistance in making these determinations.

⁵ Kohlrausch, Z. physik. Chem., 64, 134 (1908).

thoroughly, after which the maximum conductivity was reached in from two to ten minutes. The conductivity then gradually decreased for several days. Sometimes, in order to hasten the final equilibrium, the solution was carefully filtered and coarse crystals were added. In some cases also, a few drops of conductivity water were added to the supersaturated solution in order to hasten the final equilibrium. When too much water was added the conductivity again increased to approach the normal equilibrium. This change served as a means of determining whether a solution of conductivity higher than normal at the end of a test was still supersaturated, or whether the higher conductivity was due to impurities.

Table I Solubility Values for Lead Fluoride At 25°. Size of particles 0.3μ except in No. 7 where it was about 0.2μ

	Conduc Begin,	etivity > High	< 10 ⁶⁰ End	High cond. corr. for return	High conen. ×103	High conen. corr. for return ⁵ ×10°	from grav. analysis ×10°		orease Corr.	Wt. in g. added to 50 cc.
1	513	547	523	536	6.02	5.88		8.5	6	0.06
2	513	555	524	544	6.14	5.99		10.6	8	0.05
3	513	549	515	548	6.07	6.03		9.4	8.7	0.1
4	513	547			6.03		5.99	8.7		
5	513	545			6.00		6.00	8.1		
6	(H_2O)	541	516	538	5.93	5.90		6.9	6.3	0.3
7	582	590°	538	565		6.28			13.1	0.025
8	543	557°	521	549		6.06			9.2	0.13
				(16	ess than	1)	(less tha	n)	
9	598	581^{c}	543	550	6.32	6.07		13.8	9.4	0.3

 $^{^{\}circ}$ A water correction not greater than 2 \times 10 $^{-\circ}$ was applied to the saturated solutions to bring them to the value determined gravimetrically as correct (0.00555 gramequivalents per liter).

In Table I are tabulated the most reliable data obtained on the increase in solubility of lead fluoride. In the first three experiments, the fine powder was added to the saturated solution and the solution kept until the conductivity had again decreased to a point where it was constant. In Expts. 4 and 5 the solution was filtered as soon as possible after the addition of the fine powder and the concentration also determined by gravimetric analysis. In No. 6 the powder was added directly to water and the solution observed until it had returned nearly to the saturated value. In Expt. 7 a supersaturated solution was prepared by heating a solution to boiling with an excess of crystals and filtering the liquid into the cell. Fine

^b When the supersaturated solution in contact with crystals failed to return to the conductivity value corresponding to a normal saturated solution, the presence of impurities was indicated. On this assumption, therefore, in columns marked "Corr. for return" a correction equal to the difference between the beginning and end solutions has been subtracted from the high value.

Five minutes after adding powder.

powder was then added and the conductivity found to increase slightly and then decrease to a value considerably below the starting point. This showed that the solution was not sufficiently concentrated to be in equilibrium with the finest particles present. The final conductivity when the solution became constant indicates considerable contamination, due either to increased hydrolysis at the higher temperature or to impurities acquired during the boiling and filtering. The increase calculated after applying corrections is high, but the powder was an unusually fine sample.

No. 8 is very similar to No. 7, except that the original solution was less concentrated and the maximum concentration reached was lower. In the case of No. 9, the original solution was more concentrated than a solution in equilibrium with the powder. This, therefore, sets an upper limit on the maximum increase in solubility for a powder of the size used. In a similar experiment not tabulated, an increased concentration of 20% was found to be much too high and a very rapid decrease occurred upon addition of the powder. It is interesting to note that the concentration reached five minutes after addition of the powder is approximately the same in No. 8 as in No. 9 although the point was approached from different directions.

Nine per cent. has been taken as the value representing the increased solubility of lead fluoride powder 0.3μ in diameter. Working with a saturated solution of lead fluoride in 95% alcohol, an effect of about the same magnitude was found.

Lead Todide

Lead iodide gave a very small increased solubility effect. It is soft and flaky and is difficult to grind into a fine powder, even with the aid of fine quartz. The smallest particles were about 0.4μ in diameter. In two minutes an increase in concentration of about 2% was obtained.

Strontium Sulfate

Small particles added to solutions of strontium sulfate failed to disappear and allow the solution to return to the normal equilibrium. This may be due partially to a very slow rate of solution in this case, but similar difficulties occurred and are discussed in greater detail in connection with barium sulfate. While an initial increase as high as 25% was obtained for particles $0.3\,\mu$ in diameter, there was never more than a 2% return from the maximum.

Silver Chromate

A precipitate composed of good orthorhombic crystals from 10 to 50μ in length was made by mixing very dilute hot solutions of silver nitrate and potassium chromate. The crystals were easily ground. The average size of the small particles was considered to be 0.3μ . The solutions were constant in cells with bare electrodes, but the conductivity of a saturated solution decreased when put into a cell with platinized electrodes. After

adding 0.35 g. of powder to 500 cc. of solution and stirring the mixture with pure air, 24 hours was required to reach a maximum conductivity. The resulting solution when pipetted into another cell and stirred in contact with coarse crystals by means of a platinum paddle-wheel stirrer showed a decrease in conductivity for three days. After this time a slight but gradual increase set in, probably due to contamination of some kind. Two experiments at 26° agreed very closely, the fine powder causing an increase in equivalent concentration from 0.192×10^{-6} to 0.218×10^{-6} , or 13.5%, and the return in three days was 7%. In view of possible contamination or decomposition affecting the conductivity, 10% seems to be the most reasonable estimate of the real increase.

Calcium Fluoride

In one experiment pure mineral fluor spar was used. For the others, c.p. calcium fluoride was ground fine and digested several times with water until only coarse crystals remained. In some cases the powder was all added at once, and in other cases at intervals until no more effect was noticed on further addition. The time required for the powder to produce a maximum conductivity was usually from three to five minutes, but in one case was 24 minutes. This was followed by a decrease for about five days with all the solid added still present. With four experiments the increases were 24%, 19%, 32% and 29%, and the subsequent decreases were 10.5%, 15%, 12% and 17%. Considering the possible influence of impurities on the conductivity and the slow digestion back to the normal value the real increase in concentration for a given powder cannot be more than the original increase nor less than the return. Therefore, 18% is taken as the value for use in calculating the surface energy. The size of the finest powder was 0.2μ – 0.3μ with some larger particles.

Barium Sulfate

The method used for strontium sulfate was not successful with barium sulfate, because of the failure of the fine particles in the solution to disappear or grow to a larger size in any reasonable length of time.

Instead, a highly supersaturated solution (at 30°) in which the barium sulfate did not precipitate was prepared by mixing approximately equivalent quantities of very dilute sulfuric acid and barium hydroxide. The conductivity of this solution was constant at 21.4×10^{-6} . Fine barium sulfate, 0.2μ in size, was added, whereupon the conductivity fell in five hours to 16×10^{-6} where it remained practically constant for three days. Some of the clear solution was then pipetted into another cell and large crystals, 2μ – 20μ , were added. The change was slow, but in three days the conductivity fell to 12.9×10^{-6} . If it is assumed that the correction for water and impurities, such as excess acid or base, is 9.3×10^{-6} (the difference between the last value and the normal value for a saturated solution).

the solubility of particles $0.2\,\mu$ in diameter is 90% greater than that of the larger crystals.

Failure of Particles to Disappear or Grow

Attention has just been called to the failure of small barium sulfate particles to dissolve. This was also true of all the other substances studied, although to a more limited extent. Whenever, upon addition of a finely powdered substance to its saturated solution, the conductivity had gone up and then had slowly returned to its initial normal value, the expectation was that all of the smaller particles had dissolved and crystallized from the supersaturated solution onto the large crystals present. But this is not what happened. Particles were left in the solution at the end, which were just as small apparently as those present at the beginning, and these small particles, even though in intimate contact with large crystals, showed no tendency to dissolve. Frequently, large crystals formed in solution without seeding, starting with small uniform particles, as in the case of lead fluoride; but here, too, at the end of the process many small ones remained.

These facts indicate either that a large part of the increased solubility is due to particles in the powder too small to be seen and measured, or soon after entering the solution the increased solubility of the small particles is decreased by some adsorption effect such as the acquisition of a charge. The latter explanation seems more in harmony with the facts.

This effect was shown in a striking manner by the behavior of barium sulfate particles. Several very fine precipitates were made from barium hydroxide and sulfuric acid. One sample was made 0.1 N acid, one alkaline to the same degree, and the others were neutral. The precipitates were not retained by a filter, did not settle for several hours, and under the microscope most of the particles appeared to be 0.2μ – 0.3μ or less in size. After standing for three months and being frequently shaken, they could be filtered, but under the microscope most particles still appeared to be as small as 0.3μ and certainly few, if any, were larger than 0.5μ . One of the samples was then boiled under a reflux condenser for a week with no visible change even when seeded with large crystals. The particles were found to have a negative charge as they migrated very definitely in a U-tube under a potential of 125 volts.

When 10 cc. of concd. hydrochloric acid was added to 100 cc. of the suspension and the boiling continued, a marked change took place. After a few hours particles several microns in length appeared, and after four days all particles were at least $1.5\,\mu$ and some were as large as $3\,\mu \times 10\,\mu$.

If the growth of large particles at the expense of the smaller ones is a surface-energy effect, then the hydrochloric acid must act either to increase the surface energy at the solid-liquid interface, or else to remove those interfering factors which previously had prevented the normal surface energy from exerting its influence.

If we consider only the Ostwald-Freundlich equation, the calculated increase in solubility as particles become very small is so large that it seems improbable, and we are led to believe that some other factor enters to prevent actual attainment of the solubility predicted. W. C. M. Lewis⁶ has proposed an expression, also independently developed and extended by Knapp, which is based on the assumption that an electrical charge present on the surface of a small particle would decrease the solubility of such a particle. The curve plotted by Knapp from his equation shows that after a certain decrease in size a maximum solubility is reached, and for smaller particles the solubility is again diminished as we pass into the region of colloids. It seems probable that such a charge, by decreasing the surface energy and thus diminishing the increased solubility, may bring about a condition of equilibrium and prevent the further growth of particles at any size between those of a stable colloid and coarse crystals. If this is true, then the increased solubility for a definite size of particle would depend largely on conditions in the solution, and surface-energy calculations based on a solubility increase may be in error from this cause.

Calculation of Surface Energy.—By substituting the data giving the solubility of different sized particles in the equation⁸

$$\sigma = \frac{i RTr \rho \ln \frac{Sr}{S}}{2M} \tag{1}$$

it is possible to calculate the surface energy at the solid-liquid interface. It is evident, however, that all data obtained so far, including those of the

Table II

Calculated Values for Surface Energy

				Diam. of particles	% Sol.	Temp			
Substance	Mol. wt.	Density	Mol. vo	ol, µ	increase	°C.	· i	σ	Hardness
PbI_2	461.04	6.16	74.8	0.4	2	30	1.97	130	very soft
CaSO _{4.2} H ₂ O ^a .					4.4-12	30	1.56		1.6-2
Ag ₂ CrO ₄					10	26	1.95		about 2
PbF ₂	245.20	8.24	29.7	0.3	9	25	1.70	900	about 2
SrSO ₄					26	30	1.82		3.0-3.5
BaSO ₄ b	233.43	4.5	52	0.1	80	25	1.96	1250	2.5-3.5
				(Hulett)					
	233.43	4.5	52	0.2	90	30	1.96	3000	2.5-3.5
CaF ₂	78.07	3.18	24.6	0.3	18	30	1.97	2500	

^a See previous paper (Ref. 2) for discussion.

^b The reason for the large difference in the two values of σ lies in the difference in the estimated size of the particles.

Lewis, Kolloid Z., 5, 71 (1909).

⁷ Knapp, Trans. Faraday Soc., 17, 457 (1922).

⁸ For a discussion of this equation see the previous paper, Ref. 2.

present paper, are liable to so many errors that such calculations cannot be made with any great degree of exactness. In fact, besides the charge effect, the unknown shape of the fine particles, the errors in measurement of their size, the different rate of solution of different crystal faces, and the influence of crystal habit on the immediate growth of the particles, are certainly factors which interfere very seriously with the applicability of an equation based on the assumption that particles are spherical with uniform surfaces. However, the values for surface energy in Table II are the most nearly correct that can be obtained from data available at this time.

It will be seen that there is a rough proportionality between surface energy and hardness, as might be expected. It is further evident from Equation 1 that, other things being equal, the surface energy should vary directly as the density and inversely as the molecular weight; in other words, the surface energy should vary inversely as the molecular volume. This general relation is indicated by the table. However, the solubility increase varies greatly with different substances, and it is evident that such a relation can hold only for substances of the same general type.

This inverse relation between surface energy and molecular volume is approximately true for the fused lithium, sodium, potassium, rubidium and cesium compounds of fluorine, chlorine, bromine and iodine, and their nitrates and sulfates. Of all these alkali salts lithium fluoride has the smallest molecular volume and consequently the largest surface energy. At 1270° it is 201 ergs per sq. cm., at 1000° it is 237, and at 870° it is 250, making an extrapolated value of about 350 at 25°, for the supercooled liquid. By substituting 350 for σ in Equation 1 the calculated increase in solubility for particles of lithium fluoride 0.3μ in diameter would only be about 1%. As a matter of fact, it was not possible with the methods employed in this investigation to detect an effect with lithium fluoride as great as 0.5%, showing the very slightly increased solubility of fine powders with substances of small molecular weight.

This work was made possible through a National Research Fellowship. The author also wishes to thank Dr. Edward Mack, Jr., for his suggestions and encouragement.

Summary

- 1. A value for the surface energy has been calculated from the increased solubility of small particles for lead fluoride, lead iodide, silver chromate, strontium sulfate, barium sulfate and calcium fluoride.
- 2. It has been shown that a rough proportionality exists between surface energy and hardness, and the inverse proportion between surface energy and molecular volume, predicted by the Ostwald-Freundlich equation, has been indicated.
- ⁹ F. M. Jaeger, Verslag Akad. Wetenschappen Amsterdam, 17, 555 (1914); Z. anorg. allgem. Chem., 101, 1 (1917).

3. It has been observed that fine particles may have their solubility diminished by an electrical charge or adsorption effect on the surface.

Columbus, Ohio

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE]

THE PREPARATION OF DIPHENYL

By Carroll H. Lowe and C. James Received February 14, 1923

After the publication of a paper¹ in which the preparation of diphenyl was given, one of the present authors received several letters stating that the process failed to give good results. Since these statements were so contrary to those given in the original article, it seemed advisable to make a reinvestigation. A careful study of the faults of the first method revealed the fact that there were two striking difficulties which could be overcome only by bringing much sounder mechanical principles into play.

The first troublesome factor was the incessant short circuiting due to the expansion and sagging of the Nichrome ribbon filament, when heated. The second element of trouble was that due to superheating at the points where the filament came in contact with the means of support.

Description of the New Apparatus

As in the old, the new apparatus consisted of a 12-liter Pyrex flask, supported by a tripod. In the neck of the flask a tightly fitting stopper was inserted, through which a hole had been bored for the delivery tube of the inverted condenser. The latter was retained in a perpendicular position by means of an iron stand and clamp. In addition to the hole for the delivery tube, three symmetrically placed, very small holes were bored, through which passed the rods of the internal mechanism. Their purpose was to serve as threaded axes of the necessary binding posts for the essential electrical connections.

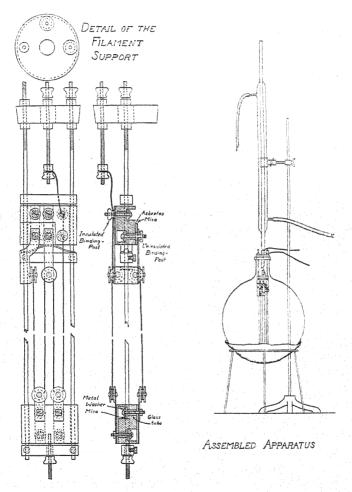
As has been previously mentioned, the problem was mainly one concerning an adequate filament support. After considerable experimentation, a type that was highly satisfactory was devised, all the faults of the old process being completely eliminated. The main supports consisted of two parallel steel rods, threaded on the ends that passed through the cork. These were securely retained in position by three steel cross-braces, two of which were held firmly in place by set screws.

Two larger blocks of steel were grooved on the edges and placed between the rods. This allowed the former to slide up and down, easily, as far as the cross-braces would permit. Between the middle cross-brace and upper block a powerful, arched strap spring of steel was inserted.

¹ This Journal, 39, 933 (1917).

Through the center of the lower cross-brace, a 6mm. hole was bored. This allowed free passage of the threaded steel wire which was screwed into the lower block, parallel to the main supporting rods.

On the opposite end of the threaded wire was an adjusting screw, the purpose of which was to secure the desired tension on the filament before



use. Once the filament was in position, it became an easy matter to tighten it, and the resulting tension would cause a depression of the arched spring. Upon passage of the electric current through the filament the expansion which took place was taken up by the tendency of the depressed spring to assume its former position, thus keeping the filament taut at all times. This removed the possibility of short circuiting and eliminated one of the main difficulties of the old apparatus.

Instead of using a 4-stranded filament as formerly recommended, one of S strands was used, thereby doubling the heating surface. This filament did not reach a higher point than the base of the neck of the flask.

On each of the movable blocks were brass, flanged discs over which the filament passed from strand to strand. This method of holding the filament in place did away with the troublesome superheating and prevented any danger of breaking due to sharp cornered hooks.

One of the special features in this apparatus is the method of insulating the flanged discs against contact with the blocks themselves. The details of this, however, are much better given by the accompanying drawings than could be attempted in words. Whatever specifications are lacking above will be found clearly indicated in these drawings.

Precautions

In attempting to run this new process a few precautions are absolutely necessary.

To begin with, the operator must never lose sight of the fact that it is a very dangerous procedure to attempt heating the filament, to incandescence, until all of the air within the flask has been expelled. Should any oxygen be present, it will promote combustion of the benzene and a very serious explosion may result. As a measure of additional safety, it is highly advisable to install an automatic cut-off, in case the current is temporarily shut off.

Care must be taken not to over-heat the filament; it should be maintained at a yellowish-red tinge. Under the best conditions a mist forms, the benzene returning from the condenser has a yellowish color and diphenyl streams down the sides of the hot flask. Formation of carbon at different points will give a warning of over-heating. It should be remembered that no part of the filament ought to be in the liquid phase. If the bottom of the lower block just touches the surface of the liquid, sufficient heat will be transmitted through it to keep the liquid boiling.

It is highly advisable to keep the filament at an even temperature throughout the entire run, although it will not break should it be cooled a few times. It is only a matter of 5 or 10 minutes' time to replace the old with a new filament.

The mechanical parts should be cleaned often in order that the tarry residue, which is deposited all over the surfaces, may be prevented from retarding their free and easy motion. When the filament support is not in use, it should be kept immersed in a small covered container filled with benzene.

Results.—One kilogram of diphenyl has been obtained in a 24-hour run, using a current of 110 volts and 10 to 12 amperes. The amount of byproducts separated by fractional distillation is not very great.

The application of this type of apparatus for other processes, involving simple heat effect, or where the filament is covered with catalytic material such as oxides, etc., is now under investigation.

Summary

- 1. A filament support has been described which eliminates all previous difficulties in the preparation of diphenyl, such as local heating and short circuiting due to expansion and sagging.
- 2. Very good yields of diphenyl can be obtained from benzene by maintaining the Nichrome filament at a yellowish-red heat.
- 3. The benzene used was commercially pure and not anhydrous. The addition of more water did not hasten the reaction.

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[Contribution from the Soils Laboratory, Agricultural Experiment Station, University of Missouri]

THE NATURE OF THE ACIDITY OF THE COLLOIDAL CLAY OF ACID SOILS

By Richard Bradfield

RECEIVED MAY 11, 1923

The problem of soil acidity has probably been investigated more than any other one soil problem, but in spite of the vast amount of work that has been done there is still considerable doubt as to its real nature.

Fisher¹ in his excellent résumé of the subject concludes: "It cannot be said that the enormous amount of work done has either solved the practical problem or clarified our ideas as to what exactly soil acidity means."

The earlier chemists believed with Sprengel² that soil acidity was due to the accumulation of complex insoluble organic acids. Recent work by Odén,³ using electrochemical methods, has established the validity of Sprengel's contention when applied to soils high in organic matter. Some of our most acid soils, however, are very low in organic matter and their acidity must be due to some other cause. If aqueous extracts of most acid soils are boiled to expel the carbon dioxide they will not as a rule be sufficiently acid to redden litmus paper even though the moist soil itself may change it almost immediately. This and similar observations led to some doubt as to the existence of real acids in soils and to the idea of "negative acidity." The conception of "negative acidity" had its origin in the work of Van Bemmelen who found that certain colloids and soils exhibited a preferential absorption for bases when treated with neutral salts, leaving the solution acid. This idea was developed into the selective adsorption theory of soil acidity by Cameron, Parker, Harris and others. 4 Ramman discarded the expression

¹ Fisher, J. Agr. Sci., 11, 20 (1921).

² Sprengel, Archiv. Ges. Naturl., 8, 145 (1826).

² Odén, Trans. Faraday Soc., [2] 17, 288 (1922).

⁴ Cameron, J. Phys. Chem., 14, 320, 393 (1919). Parker, J. Agr. Res., 1, 179 (1913).
Harris, Mich. Expt. Sta. Tech. Bull., 19 (1914). Ramman, "Bodenkunde," J. Springer, Berlin, 1911.

"acid soils" using instead "absorptively unsaturated soils." Salter and Morgan⁵ in a recent study of the effect of the soil-water ratio on the Sörensen value of acid soils, found that the relationship was logarithmic and could be expressed by the usual absorption isotherm. They concluded that their data "discredit any theory of soil acidity which assumes that the acid reaction is due to highly insoluble acids, organic or inorganic which must under conditions of equilibrium form a saturated solution and give a constant Ph."

A great number of the recent workers on soil acidity believe, nevertheless, in the existence of highly complex insoluble alumino-silicic acids. This theory proposed by Loew in 1913 has been substantiated by the work of Ashley, Mellor and Clark⁶ on the constitution of pure clays, and by Truog⁷ who worked with agricultural soils. Soil chemists are practically unanimous in the opinion that the condition called "soil acidity" is due to a removal of the soluble bases by prolonged leaching. Since soils are composed of complex minerals, which are salts of strong bases and weak acids, it is to be expected that they would hydrolyze slowly, producing soluble bases which would be leached away by the rains and the insoluble acid residue would remain in situ to accumulate as the weathering proceeded. MacIntire⁸ points out that the degree of acidity of a soil is closely correlated with its degree of hydration.

The principal arguments against the true acid theory are (1) that equivalent quantities of different bases are not taken up by soils, (2) that the titration curves of soils by bases show no breaks corresponding to neutral points but are almost linear. Truog' found however that, if experimental conditions were adjusted so as to keep side reactions at a minimum, equivalent quantities of bases were taken up by soils. The absence of breaks in the titration curves may be due, as will be shown later, to the fact that such titrations are usually made by adding increments of the standard base to a definite quantity of the acid soil. This is quite contrary to the teachings of physical chemistry. If a sharp end-point is desired the weak acid should be added to the strong base.

A survey of the literature on soil acidity shows that the following points are very well established regardless of the nature of the underlying causes.

- 1. Natural soils vary in Sörensen (PH) value from about 3.5 to 9.5.
- 2. Aqueous extracts of acid soils when freed from carbon dioxide are usually acid-free.
- 3. Extracts of acid soils made with neutral salt solutions show a higher Sörensen value than the soil, and also considerable titrable acidity.
- 4. Titration curves, made by adding increments of bases to a fixed weight of soil and determining the corresponding Sörensen values show no definite breaks to indicate end-points, but are almost linear.
- 5. The slope of the curve varies widely with soil type. It is usually inversely proportional to the content of colloidal material. In other words the buffer action of a soil is some direct function of its colloid content.

Principles Underlying the Present Investigation

Soils are complex systems with particles ranging from a few millimeters in diameter down to molecular dimensions. The rate at which a

- ⁵ Salter and Morgan, J. Phys. Chem., 27, 123 (1923).
- Loew, Porto Rico Agr. Expt. Sta. Bull., 13 (1913). Ashley, Bur. Standards. Tech. Paper, 23 (1913). Mellor and Holdcroft, Pot. Gaz., 36, 680 (1911). Clark, U. S. Geol. Surv. Bull., 588 (1914).
 - ⁷ Truog, J. Phys. Chem., 20, 457 (1916).
 - · 8 MacIntire, J. Am. Soc. Agron., 13, 157 (1921).

chemical reaction proceeds increases with a decrease in the size of the reacting particles. It is to be expected then that the more finely divided colloidal material in soils would reach an equilibrium much more quickly than the non-colloidal fraction. The situation is probably complicated still more in soils by the fact that the colloidal fraction forms a coating over the coarser particles which would tend to protect them. Because of this complexity of the soil system it would seem logical to use a physically homogeneous fraction for studies of the nature of the acidity. Since the buffer action of soils is closely correlated with their colloid content, the colloid fraction would seem to be the one best adapted for such studies. It has the additional advantages of having a high specific surface and of being accurately measurable by means of ordinary pipets and burets, which greatly facilitates titrations.

The end-point in the titration of colored solutions can readily be determined by conductivity measurements. The conductivity is at a minimum at the neutral point in the case of the titration of a strong base by a strong acid, and it makes little difference in that case whether the acid is added to the base or the reverse. If, however, a strong base is being neutralized by a weak acid the conductivity curve shows no increase after the neutral point is reached, but remains practically constant. If the process is reversed, and the strong base added to the weak acid, which is the method usually followed in soil investigations as pointed out by Findlay, "The minimum will not be sharp owing to the fact that the change in conductance is not due so much to the disappearance of the fast-moving hydrion (which is present in comparatively small concentration) as to the replacement of the un-ionized acid molecules by the ions of the salt formed."

A similar situation exists in making a titration curve by means of the hydrogen electrode. In order to obtain distinct breaks at the end-points of the titration the amount of buffering substances should always be kept at a minimum. This can be done by titrating the strong base with the weak soil acid. In the work of Knight, Spurway, and Stevenson, in increments of the standard alkali solution were added to fixed quantities of soils. Under such conditions a maximum amount of either the weak soil acid or its salt is always present, exerting so great a buffer action that these investigators find an almost linear relationship between the amounts of base added and the increase in Sörensen value produced.

In this investigation standard solutions of sodium hydroxide and calcium hydroxide were titrated with the colloidal material from four acid

⁹ Findlay, "Practical Physical Chemistry," Longmans, Green and Company, London, 1911, p. 180.

¹⁰ Knight, J. Ind. Eng. Chem., 12, 465 (1920). Spurway, Mich. Agr. Expt. Sta. Tech. Bull., 57 (1922). Stevenson, Soil Science, 12, 145 (1921).

soils and the end-points located by both conductivity and hydrogen-ion concentration measurements.¹¹

Experimental Part

The colloidal clay was extracted from the heavy sub-soils of the Marion, Cherokee, Putnam and Robertsville silt loams, each of which is very acid and very low in organic matter, by the method developed in this Laboratory. The solutions used contained 1 g. of oven-dried material per 100 cc. except in the case of the Robertsville, which contained 2 g.

Preliminary trials indicated that the basic solutions should have a normality of the order of $0.01\ N$. Ten cc. of $0.01\ N$ base was placed in a $100{\rm cc}$, graduated flask by means of a pipet and the desired quantity of the 1% colloidal clay solution added. Enough neutral distilled water was added to bring the volume up to $100\ {\rm cc}$. (except in the case of the additions of $100\ {\rm cc}$. or over). After the solutions were thoroughly mixed, they were poured into $100{\rm cc}$. florence flasks which were kept stoppered to minimize contamination by carbon dioxide. About $15\ {\rm minutes}$ after mixing, a portion of the mixture was used for a hydrogen-ion determination. These determinations were made with a standard potentiometer, using the saturated potassium chloride calomel electrode and a modification of the Hildebrand type of hydrogen electrode. The temperature varied only slightly from $25\ {\rm ^\circ}$.

The conductivity measurements were made by the usual bridge method, using a Washburn Type B cell, a microphone hummer as a source of alternating current and a tunable telephone receiver to indicate the point of balance. The resistance was kept constant at 9999 ohms and the results are reported as bridge readings. The potentiometer was used as a bridge. The bridge wire was 1100 units long. The temperature was maintained at 25° \pm .02 by a small thermostat.

Experimental Results.—The 1% stock solutions of the colloidal clays gave the conductivities and Sörensen values shown in Table I.

TABLE I

CONDUCTIVITY	and Sörensen	VALUES OF	1% COLLOIDA	L CLAY	Solutions
Soil			E.m.f.	$P_{ m H}$	Bridge reading
Putnam			0.498	4.30	935
Cherokee			520	4.65	990
Marion			506	4.42	1007

The rate of reaction between the colloidal solutions and the bases was studied by mixing the two in the desired proportions as usual, then determining the conductivity at frequent intervals. Equilibrium was attained almost instantly. Bridge readings taken as soon after mixing as possible were almost identical with those taken after standing overnight.

¹¹ THIS JOURNAL, 45, 1245 (1923).

The titration curves for the Putnam and Cherokee clays obtained by both the conductivity and hydrogen electrode methods are given in Fig. 1. The curve for the Marion clay was almost identical in type with the Putnam and is for that reason omitted. About twice the usual quantity of base was used in the curve for the Robertsville clay (III) in order to place

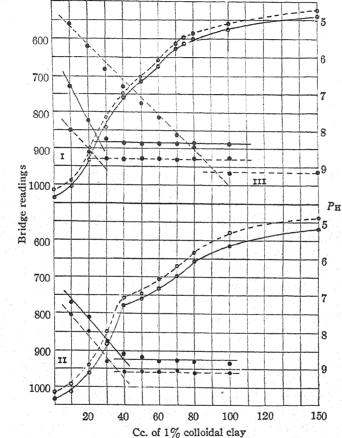


Fig. 1.—Titration curves of Putnam clay (I), Cherokee clay (II), and Robertsville clay (III). Circles represent hydrogen-electrode curves; dots, conductivity curves. Broken lines denote that Ca(OH)₂ was the base used; continuous lines, NaOH

more points on the slanting portions of the curve. (A 2% solution of the Robertsville clay was used and the results plotted on the 1% basis.) The conductivity curves are all of the type commonly obtained in the titration of a strong base by a weak acid. As the strong base is neutralized and replaced by the comparatively insoluble salt of the alumino-silicic acid, the conductivity decreases linearly. After all of the base has been neutralized, the conductivity becomes constant and the addition of an excess

of the weak colloidal acid has no effect. If we were dealing with an adsorption of the type expressed by Freundlich's isotherm instead of a neutralization, we should expect the curve to continue to drop in a logarithmic fashion until the value of the colloidal clay was approached. The curves obtained with calcium hydroxide approach this point, as would be expected from the low solubility of the calcium silicates and from the differences in the mobilities of the calcium and hydrogen ions but the minimum conductivity obtained with sodium hydroxide was in every case considerably higher than that of untreated clays; increasing the amount of clay almost four times after this minimum had been obtained failed to reduce the conductivity further. This would seem to indicate that in this case either we have an ordinary neutralization with the formation of the sodium salt of the acid which is more soluble than the acid itself, or from the adsorption point of view the colloidal clay regardless of the amount present is unable to adsorb the sodium beyond a certain critical concentration. Adsorptions are usually characterized by the lack of stoichiometric relations between the quantities of different bases taken up. In the conductivity curves of all the clays studied the two linear portions of the curves intersect at a point (the end-point) which corresponds to approximately the same amount of acid regardless of the nature of the base, which would seem to be rather conclusive evidence of the stoichiometric character of the reaction.

The curves obtained with the hydrogen electrode are also of the type commonly obtained in the neutralization of a strong base by a weak acid. The flatter portion of the curves in the most alkaline region is not as pronounced as in most titration curves, probably due largely to the great dilution of the standard alkali used (0.001 N after dilution). There is in each case a slight change in the slope of the curves at about PH 7. This break is especially marked in the case of the Cherokee and indicates that there may be at least two distinct dissociation constants involved. The curves gradually flatten as an excess of the colloidal acids is added and approach the Sörensen value of the pure acids. The curves for sodium hydroxide follow those for calcium hydroxide very closely, confirming the conductivity curves, but show always slightly more alkalinity. This is doubtless due partly to differences in the solubility and hydrolysis of the salts formed and partly to a slight difference in the concentration of the basic solutions used. The sodium hydroxide solution was slightly over 0.01 N (0.0105) and the calcium hydroxide solution was not quite 0.01 N (0.0099). This difference when calculated to equivalents of the colloidal acids makes a difference of about 1.8 cc. of the 1% solutions.

The end-points of the titration obtained by the two methods (the intersection of the linear portions in the case of the conductivity curves and the midpoint of the steep portion of the curve in the case of the PH curves) lie as close together as could be expected with a weak acid of this type.

About 37 cc. of 1% Cherokee, 27 cc. of 1% Putnam, and 37 cc. of 1% Marion soil were required to neutralize 10 cc. of the 0.01~N bases. This gives the 1% solutions of the acids about the following normalities, Cherokee 0.0027, Putnam 0.0037 and Marion 0.0027.

Discussion of Results

The chief objections to the chemical theory of soil acidity are (1) no one has ever been able to isolate an undeniable acid from a soil in quantities commensurate with the soil's "sourness;" (2) acid soils do not absorb bases in equivalent quantities; (3) titration curves made by titrating a comparatively large mass of soil with a base are practically linear, showing no break such as is characteristic of true neutralizations.

The results obtained in this investigation tend to show that the colloidal material of an acid soil is itself an acid which ionizes to produce a definite Sörensen value and which shows a definite titrable acidity or normality on titration with strong bases. The fact that the acid is colloidal explains why it is not found in colloid-free aqueous extracts. Soils investigators have as a rule been expecting to obtain a negative ion of the soil acid which would be of the same dimensions as the ordinary crystalloid ion. This could hardly be expected if we consider the great complexity of the minerals which are found in soils. It would seem much more logical to expect the anion of the soil acid to be very large and complex, even reaching colloidal dimensions.

It has long been known that clay particles when suspended in water and placed in an electrical field migrate to the anode. Recent measurements in this Laboratory show that the velocity of migration of the colloidal particles is of the same order of magnitude as that of the average slow moving ion of crystalloids. This shows that the particles have an electric charge of the same order of magnitude as that of the crystalloid ion. This charge has commonly been ascribed to the preferential adsorption of hydroxyl ions by the colloidal particle. If the excess of hydrogen ions in the colloidal clays studied is due to the ionizing of the colloidal particles themselves, as this work indicates, then an equal negative charge must remain on the residual colloidal particle. These charged colloidal particles would be in reality very large complex negative ions, as the cataphoresis experiments indicate. This view is in harmony with the findings of Loeb, Pauli, Michaelis, Sörensen and others in their investigations of colloidal protein solutions and with the work of McBain on colloidal electrolytes.

The results obtained by Salter and Morgan⁵ which are discussed above would be expected if they were dealing with a colloidal acid. Their argument in favor of the adsorption theory is based on their belief that

¹² Russell, "Soil Conditions and Plant Growth," Longmans, Green and Co., London, 1921, p. 110.

they were dealing in all the soil-water ratios studied, with a saturated solution. This fundamental assumption is not necessarily true. Their belief that they were dealing with a saturated solution was apparently based upon the fact that there always remained a certain amount of the solid phase undissolved. A considerable portion of most soils is made up of rather coarse particles of minerals such as quartz which are very inactive. The amount of colloidal material is in most cases comparatively small. so small as to make it seem highly improbable that the solution was saturated even with a ratio of 1 part of soil to 1 part of water. Their curves began to flatten, however, in the most concentrated mixtures, which indicates that they were probably approaching a concentration in which the Sörensen value would become constant. Any weak acid will yield a logarithmic curve for certain concentrations when its hydrogen-ion concentration is plotted against its concentration. The curve becomes linear only when the acid is completely dissociated at infinite dilution. The curve of Salter and Morgan becomes practically linear at the point corresponding to 100 g. of soils to 1000 cc. of water which indicates that they have reached a concentration corresponding to infinite dilution at that ratio. Instead of discrediting a colloidal acid theory of soil acidity, their results would seem to be exactly what would be expected from such a theory.

The second objection to the true acid theory of soil acidity is that equivalent amounts of bases are not removed. As pointed out above such results have usually been attained when a relatively large ratio of soil to reacting base was used. Such conditions favor complex side reactions in which the solubilities of the resulting salts play a role. Truog has shown that if a small sample of soil is treated with a large excess of the base or salt, conditions favoring the direct action and unfavorable to the side reactions, approximately equivalent quantities of bases are taken up. In this investigation the same end was accomplished by adding small increments of the colloidal acid to a definite quantity of strong bases. The titration curves for calcium and sodium hydroxides in each case lie so close together that if we take into consideration the differences in the solubilities of the alumino-silicates which are indicated in the conductivity curves, there can be little doubt that equivalent quantities of the two bases are neutralized by the colloidal acid.

The third objection, that soil titration curves do not exhibit definite breaks, has been shown to be unfounded provided that the strong base is titrated with the weak soil acid. With the reverse procedure, which is usually followed in soil investigations, an excess of the weak acids and their salts, the substances responsible for the high buffer action are present from the start and tend to obscure the breaks normally expected. The end-points found by the conductivity method are as sharp as those commonly obtained with weak acids.

The curves obtained by the hydrogen-electrode method are also of the type usually obtained with very weak acids. There are no sharp breaks, but the slope changes gradually, showing the least buffer action between PH 9.5 and 7. At the latter point there is a slight flattening of the curve with all clays studied. This flattening is more marked with the Cherokee soil than with any of the others (Fig. 1, II). It seems to be as pronounced as that observed in the titration of certain weak crystalloidal acids such as phthalic acid¹³ and would seem to be evidence that at least a dibasic acid was involved. It would be difficult to account for such a change by the adsorption theory but it is exactly what would be expected if we were dealing with a true neutralization of a base by a weak polybasic acid.

There yet remains the possibility that the acidity neutralized is due to acids other than alumino-silicic. As pointed out above, the colloids used in this study were extracted from the sub-soils of four soils very low in organic matter. They were likewise very low in phosphate and sulfate. The percentages of these substances were so low and the quantity of colloidal acid used so small as to render it inconceivable that the acidity found was due either to organic acids or to traces of the more common strong inorganic acids.

In spite of the strong acidity of the soil colloids and of the fact that the colloid content of soils is much higher than is commonly believed, as has been shown by the recent work of Moore, Fry and Middleton¹⁴ and confirmed in this Laboratory, it is not believed that such acidity accounts for all the acidity of sour soils. The exteriors of the larger non-colloidal particles of such soils have doubtless lost considerable of their bases. The work of Brown and Johnson, Truog¹⁵ and others indicates that the interior of such particles when freshly exposed to the solvent action of water after thorough grinding may contain enough soluble bases to render the solution alkaline in reaction. Such particles are probably responsible for most of the so-called latent acidity, since the results obtained in this investigation indicate that the reaction of the colloidal material is very rapid.

Additional evidence in favor of the true acid nature of acid colloidal clays is found in the studies previously reported, ¹⁶ in which it was found that the concentration of potassium ions required for complete flocculation of the acid clay increased about 10-fold when the Sörensen value was raised from 6.5 to 8.5, and then became constant, indicating that after a sufficient concentration of hydroxyl ions to neutralize the acid has been added further increases (almost a thousand-fold) are without effect.

¹⁸ Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1920, p. 191.

¹⁴ Moore, Fry and Middleton, J. Ind. Eng. Chem., 13, 527 (1921).

¹⁵ Brown and Johnson, ibid., 7, 776 (1915). Ref. 7, p. 478.

¹⁶ Bradfield, This Journal, 45, 1243 (1923).

Other studies on the variation of the hydrogen-ion concentration of the acid clays upon dilution gave curves apparently identical in type with those obtained with weak acids such as acetic acid.¹⁷

Summary

- 1. Solutions of calcium and sodium hydroxides were titrated with 1% solutions of four subsoil colloidal clays. The end-points found by both the conductivity method and the hydrogen electrode were fairly definite and the curves were of the type usually obtained in titrating a strong base with a weak acid.
- 2. The same amounts of the colloidal acids were required to neutralize equivalent quantities of the two bases.
- 3. Definite breaks were found in the conductivity curves, indicating the neutralization of definite acids which in 1% solutions had concentrations ranging from 0.0027 to 0.0037 N.
- 4. The reaction between acid colloidal clays and strong bases seems to be an ordinary neutralization. Recourse to the adsorption theory seems unnecessary.

COLUMBIA, MISSOURI

[Contribution from the Laboratory of Physiological Chemistry, University of Iowal

STUDIES ON ENZYME ACTION. THE RELATIONSHIP BETWEEN THE CHEMICAL STRUCTURE OF CERTAIN COMPOUNDS AND THEIR EFFECT UPON THE ACTIVITY OF UREASE

By Elbert W. Rockwood and William J. Husa Received June 29, 1923

Various organic compounds have been reported as influencing the activity of urease.¹ Lövgren² gives a rather full review of the general properties of urease and includes a bibliography containing over 200 references. From his review of the literature Lövgren concludes that all the promoters³ are weak acids of amphoteric electrolytes, and that their accelerating influence lies in their checking of the PH increase.

- 17 Bradfield, paper to appear in J. Phys. Chem., 1923.
- (a) Armstrong and Horton, Proc. Roy. Soc., 85B, 109 (1912).
 (b) Armstrong, Benjamin and Horton, ibid., 86B, 328 (1914).
 (c) Marshall, J. Biol. Chem., 17, 351 (1914).
 (d) Van Slyke and Zacharias, ibid., 19, 181 (1914).
 (e) Falk, Biochem. Z., 59, 298 (1914).
 (f) Jacoby and Umeda, ibid., 68, 23 (1915).
 (g) Jacoby, ibid., 74, 105 (1916); 84, 358 (1917); 85, 358 (1918).
 (h) Bayliss, Arch. Néerland. physiol., 2, 621 (1918); through C. A., 13, 1077 (1919).
 (i) Rona and György, Biochem. Z., 111, 115 (1920).
 (j) Wester, Pharm. Weekblad, 59, 173 (1922); through C. A., 16, 1253 (1922).
 - ² Lövgren, Biochem. Z., 119, 215 (1921).
 - 3 Pease and Taylor, J. Phys. Chem., 24, 241 (1920).

It was one of the purposes of this investigation to determine whether the promoter action reported by several investigators could be entirely explained on the basis of $P_{\rm H}$ changes, or whether there was a further effect independent of this one. Provided such an effect was found; it was believed desirable to look for a possible relationship between the chemical structure of the compounds and their action on urease, and to investigate the mechanism of the action. It was hoped that such a study would throw some light on the nature of enzyme action, and at the same time would contribute to our knowledge of promoters.³

Materials Used

A solid urease preparation was obtained from jack-bean meal by the method of Van Slyke and Cullen.⁴ Urea was purified by recrystallization from ethanol. The compounds tested were obtained from reputable manufacturers, or from reliable research chemists, to whom we are indebted for compounds unobtainable elsewhere.

Experimental Procedure

Experiments were carried out with 0.1 M urea, the optimum PH of 7.5 being maintained by use of a phosphate buffer. For the controls, 5 cc. of distilled water was introduced into a 200cc. Erlenmever flask, 25 cc. of M phosphate solution (50 volumes of M dipotassium and 9 volumes of M monopotassium orthophosphate) was added, then 15 cc. of a 2% solution of urea and 5 cc. of a 0.1% solution of enzyme, making a total volume of 50 cc. In the other flasks, the compound to be tested was first placed, in amount sufficient to make 50 cc. of a 0.001 M solution. Water was added. and then sufficient alkali or acid to make the aqueous solution neutral to phenolphthalein, so that it could be more readily controlled by the buffer, the given volume of dil. potassium hydroxide or sulfuric acid solution replacing part of the 5 cc. of water. The other solutions, including the buffer, were then added as in the controls. Since light is known to hasten the decomposition of urease,2 the flasks were placed in a dark cupboard for the reaction period of approximately two hours. The variation in temperature during this time was less than 1°, and during the whole course of the work the temperature ranged from 21-28°. For analysis, a 10cc. portion of the reaction mixture was pipetted into a bottle containing 35 cc. of a saturated solution of potassium carbonate and 25 cc. of distilled water. When the action of the enzyme was thus stopped there was still an ample excess of substrate, 75 to 90% remaining unchanged. The ammonia was aerated into a mixture of 25 cc. of 0.1 N sulfuric acid and 50 cc. of distilled water and the excess acid determined by titration with 0.1 N potassium hydroxide solution, using methyl red as indicator. The time of aeration was from $3^{1}/2$ to 7 hours, depending on the room temperature.

4 Van Slyke and Cullen, J. Biol. Chem., 19, 211 (1914).

The results of Lövgren² were used in choosing the concentrations of urea and of the phosphates. According to his results for $0.1\,M$ urea and $0.5\,M$ phosphates, the formation of ammonia corresponding to $2\,$ cc. of $0.1\,N$ ammonia for each $10\,$ cc. of the mixture caused a change of $0.1\,$ Sörensen unit. Since the amount of promoter in $10\,$ cc. of the mixture corresponds to only $0.1\,$ cc. of a $0.1\,M$ solution, the difference between the control and the solution containing the added substance would thus be of the order of a few hundredths of a Sörensen unit. Thus, by neutralizing the compound to be tested and employing the $0.5\,M$ buffer, the effect of the added substance on the hydrogen-ion concentration was eliminated.

Experimental Data

Table I contains a summary of the results obtained with various classes of compounds. Table II summarizes the data on each compound tested. The activity of the enzyme in the presence of the added substances is expressed on the basis of the control taken as 100.

Table I
Summarized Results Given by Different Classes of Compounds

Class Classification	No. of compounds tested	Av. of series
I Mono-amino-monocarboxylic acids		
(a) NH ₂ in α position	10	120
(b) NH ₂ in β position		103
(c) NH ₂ in γ position		99
II Mono-amino-dicarboxylic acids	2	133
III Diamino-monocarboxylic acids	. 1	153
IV Diamino-dicarboxylic acids	1	133
V Heterocyclic amino acids	3	144
VI Derivatives of α-amino acids	3	149
VII Amines	4	98
VIII Amides	2	99
IX Other compounds	18	(See Table II)

Table II

EXPERIMENTAL DATA FROM INDIVIDUAL COMPOUNDS

	Compound d	of	COL	trol :	a basis = 100 x. Av.	of	Compound		contr	n on l	100	Av. of se- ries	
I. I	dono-amino-mono-						Histidine methyl-				,	1103	
	oxylic acids (a)						ester dichloride		150	166	159		
N	H ₂ iπ α position.,						Hippuric acid	6	132	154	143	149	
							VII. Amines						
	Glycine	10	117	142	127		Methylamine hy-						
	Tyrosine		110	145	127		drochloride		98	101	100		
	l-Leucine		111	126	118		Diethylamine hy-			101	100		
100	dl-α-Alanine	8	116	125	121		drochloride		95	96	96		
1.7	d-α-Alanine	2	124	125	124		Trimethylamine						
	Phenylalanine	4	119	125	122		sulfate		97	97	07		
	Glucosaminic						Glucosamine hy-		•				
	acid ^a	4	118	121	120		drochloride ^b		100	101	100	98	

Chondrosaminic						VIII. Amides					
acid ^a	4	114	118	115		Succinamide	6	96	100	99	
Gulosaminic						Benzamide	2	98	99	99	96
$acid^a$	4	114	121	117		IX. Other compounds					
α - Amino - n-						o - Aminobenzoic					
valeric acid	4	106	112	109	120	acid	6	100	106	103	
(b) NH2 in β posi-						m - Aminobenzoic	-			200	
tion						acid	4	97	98	98	
β-Alanine	6	100	105	102		p - Aminobenzoic	~			• •	
d - Glucosamino-						acid	4	94	97	95	
heptonic acida.	4	105	108	107		Acetyl - o - amino-	_				
l - Chondros-						benzoic acid	4	98	102	100	
amino - hep-						Acetyl - m - amino-					
tonic acida	4	96	104	100	103	benzoic acid	4	100	102	101	
(c) NH2 in γ posi-						Acetyl - p - amino-					
tion.						benzoic acid	4	100	102	100	
γ - Amino - n -						1 - Amino - 2 - hy-					
valeric acid	4	97	100	99	99	droxy - 3' bromo-					
II. Mono - amino-di-						naphthalene hy-					
carboxylic acids						drochloride	2	9	9	9	
Aspartic acid	14	132	165	150		Acetoxime	4	.69	81	75	
Glutamic acid	6	109	130		133	Betaine hydrochlo-					
	-					ride	4	97	100	99	
III. Diamino - mono-						Mueller's CoH11O2-					
carboxylic acids.						NS, from casein	4	79	89	84	
Arginine	6	137	167	153	153	Witte's peptone (10					
IV. Diamino - dicar-						mg. in 50 cc. of					
boxylic acids.			1.5			reacting soln.)	2	135	136	135	
Cystine	8	116	154	133	133	Benzoic acid	2	99	102	100	
V. Heterocyclic amino						Uric acid	2	93	95	94	
acids						Creatinine	3	98	100	99	
Histidine	6	150	170	162		Creatine	3	95	99	97	
Histidine dichloride	4	140	181	159		Guanidine acetic					
Tryptophan	4		113	112	144	acid	4	98	100	99	
		100	110			Guanidine sulfate	4	100	102	101	
VI. Derivatives of α-						Ammonium chlo-					
amino acids						ride, (results					
Asparagine	10	137	159	144		corr. for NH ₃)	4	98	100	99	

[&]quot; For this we are indebted to Dr. P. A. Levene.

Discussion

Relationship between Promoter Effect and Changes in Hydrogen-Ion Concentration.—The effects of the various added substances reported in the tables above cannot be explained on the basis of changes in hydrogenion concentration, contrary to the claims of Lövgren.² That the promoter action studied here is independent of such effects is assured by the fact that the substances tested were employed in 0.001 M concentration, neutralized and used in the presence of a 0.5 M phosphate buffer mixture.

Relationship between Chemical Structure and Promoter Effect

Are Certain Elements Essential?—In formulating a relationship between the composition or chemical structure of the compounds and their effect upon the activity of urease it may be seen at once that the action cannot be ascribed to the presence of a single element such as nitrogen, carbon, hydrogen or oxygen, nor to the mere presence of a number of elements in a compound. True, all the promoters found in our work contain ni-

b For this we are indebted to Mr. E. P. Clark.

trogen, carbon, hydrogen and oxygen, but many other compounds containing these same elements exerted no favorable action.

Effect of the Amino Group Alone.—By a further analysis of the data in terms of groups it is seen that all the promoters contain an amino or substituted amino group. That the -NH₂ group alone is not responsible for the greater action is evidenced by the results obtained with four simple amines. As shown in Tables I and II, no promoter effect was observed, the average yield of ammonia being 98% of that from the control.

Effect of the Carboxylic Group Alone.—Jacoby and Umeda^{1f} reported that no effect on the activity of urease was observed on addition of neutralized glutaric acid, COOHCH₂CH₂COOH. Our own experiments with benzoic acid, o-, m-, and p-acetylaminobenzoic acids and guanidine acetic acid also show that when care is taken to exclude changes in hydrogen-ion concentration, the carboxyl group alone has no promoter effect.

Effect of Amino and Carboxyl Groups.—Every compound which acted as a promoter contained both the amino and carboxyl groups. However, a number of compounds, both aliphatic and aromatic, containing these two groups exerted no favorable effect.

Effect of Relative Position of These Groups.—The results in Table II indicate that α -amino acids are decided promoters, β -amino acids have in some cases a slight effect, in other cases no effect, while the only γ -amino acid available had no favorable influence. In the aromatic series, the isomeric aminobenzoic acids were tested. While only the *ortho* compound showed a slight favorable effect, it seemed significant that the order was ortho > meta > para. The results with both aliphatic and aromatic compounds (although less marked with the latter) containing an amino and a carboxyl group indicate that the promoter action is a function of the distance between these groups, the stimulating effect increasing with decreasing proximity of the two groups.

Effect of Substituted Amino and Carboxyl Groups.—The methyl ester of histidine gave the same results as histidine itself, a result which indicates that esterification of the carboxyl group in a promoter does not decrease the favorable effect. Hippuric acid was a marked promoter; this result shows that the benzoyl group may replace one hydrogen of the amino group without decreasing the promoter action.

Effect of a Second Carboxyl Group and its Position.—From the data in Tables I and II it appears that the second carboxyl group slightly increases the promoter effect. In one experiment in which the two compounds were compared directly against the same control, the result for aspartic acid was 133, and that for glutamic acid 129. Since in glutamic acid the second carboxyl is separated from the amino group by one more carbon atom than in aspartic acid, it is possible that the promoter effect may depend somewhat on the proximity of the second carboxyl group.

Effect of a Second Amino Group.—A second amino group was found to increase the promoter effect. The results with arginine (guanidine- α -aminovaleric acid) averaged 153, a value which is considerably higher than the average for α -mono-amino-monocarboxylic acids.

Effect of Second Amino and Carboxyl Groups in the Same Compound.—From the results obtained with cystine it appears that the second amino group does not increase the promoter effect if there are two carboxyl groups, while a second carboxyl group does not increase the promoter effect if there are two amino groups in the compound. There is a possibility, however, that the two thio groups of cystine may influence the promoter effect.

Effect of a Heterocycle Containing Nitrogen.—Tables I and II indicate that α -amino acids having in addition a nitrogenous heterocycle give, on the average, a somewhat greater promoter effect than simple α -amino acids.

Effect of Length of Chain.—There is some indication that in aliphatic α -amino acids the promoter effect decreases with lengthening of the carbon chain. Thus the average value obtained for CH₂(NH₂)COOH was 127; for CH₃CH(NH₂)COOH, 121; and for (CH₃)₂CHCH₂CH(NH₂)COOH, 118.

Effect of Optical Isomers.—Jacoby and Umeda^{1f} working with urease without, however, eliminating changes in hydrogen-ion concentration observed no difference in action between dl-alanine and d-alanine, or between dl-glutamic acid and d-glutamic acid. In our experiments, in which effects of hydrogen-ion concentration played no part, the promoter effects of dl-alanine and d-alanine were also found to be practically equal.

Compounds Having No Promoter Action

Effect of Ammonium Chloride.—Armstrong and Horton^{1a} and other investigators have reported a favorable action of ammonium chloride on urease. In our work, changes in hydrogen-ion concentration being eliminated and correction made for the ammonia from the ammonium chloride, no such greater action has been found. Thus the favorable effect of ammonium chloride reported by others is not the specific effect demonstrated in this investigation.

Effect of Guanidine Derivatives.—Because of the apparent favorable influence of the guanidine group in arginine, other guanidine derivatives were tested. Guanidine sulfate, guanidine acetic acid, creatine and creatinine gave no promoter effect. To cover the field an amino-naphthol, an oxime and various other compounds were tried (see Table II), but no promoter effect was observed.

Effect on Activity of Enzyme as a Test for the α -Amino Group

From the results of our work it appears that the effect of a compound on the activity of urease might furnish valuable presumptive evidence as to the presence of an amino group in the α -position to a carboxyl group. An opportunity to apply this method presented itself in connection with the isolation of a new amino acid from casein by Mueller.⁵ He reported that the empirical formula of the compound was $C_5H_{11}O_2NS$, and that tests were obtained showing the presence of an amino group and a carboxyl group. The results obtained with this substance showed a depressing effect on the activity of the enzyme, the average being 84% of the controls. It would appear that this new sulfur-containing amino acid is not an α -amino-monocarboxylic acid of the cystine type.

Importance of Protein Associated with Enzymes

Enzymes seem to be of a protein nature or to occur associated with protein. When the protein is removed from an enzyme solution by coagulation with heat or other means the activity is lost. For this reason it is often stated that enzymes are proteins, or something more complex containing protein.

Van Slyke and Cullen⁴ found that their soya urease preparation contained a few per cent. of ash, the organic matter being about ²/₃ protein and ¹/₃ carbohydrate. Since three days' digestion with trypsin or papain did not markedly injure the activity of the enzyme it seemed to them unlikely that the urease was of a protein nature.

Jacoby and Umeda, If working with soya urease without controlling the hydrogen-ion concentration found the activity of the enzyme to be increased by glycyltryptophan, Witte's peptone and casein. Our experiments indicated that Witte's peptone exerts a promoter action comparable to that shown by α -amino acids.

Jacoby and Sugga⁷ reported that soya urease was not appreciably injured by dialysis, or by treatment with trypsin or papayotin. When the urease preparation was first treated with papayotin and then dialyzed, they observed a marked diminution in the activity of the urease.

Their results may be explained as follows. It has been shown that α -amino acids, peptones and proteins serve as promoters of the catalytic action of the urease. It would, therefore, be reasonable to expect a fall in activity of the enzyme preparation when the compounds containing α -amino groups are removed. Proteins being, as a rule, non-diffusible, dialysis alone might not appreciably affect the action of the urease. Further, since our work has shown that α -amino acids and peptones are marked promoters, it is evident that the breaking down of the proteins into peptones and amino acids by treatment with trypsin or papayotin should likewise not change the rate of fermentation. But if the urease preparation is dialyzed after treatment with papayotin, the protein having been changed

⁵ Mueller, J. Biol. Chem., 55, xv (1923).

⁶ Kindly furnished by Dr. Mueller.

⁷ Jacoby and Sugga, Biochem. Z., 69, 116 (1915).

into diffusible amino acids which would be removed by the dialysis, a diminution in activity of the urease should be expected. The results of Jacoby and Sugga⁷ may thus be explained on the basis that the protein part of an enzyme preparation, by its promoter action, accounts for part of the activity of the enzyme.

The Mechanism of the Promoter Effect

Various explanations have been given⁸ of the manner in which the activity of enzymes is increased by added substances. Sherman and Naylor⁹ conclude that the influence of amino acids on amylases "may be attributed either to a direct 'activating' effect dependent upon the structural nature of these substances as α -amino acids, or to conservation of the enzyme by retarding its hydrolysis."

In dealing with urease one must also consider whether an added substance such as an amino acid might not interact with the enzyme to form ammonia. Likewise, the ureolytic power of bacteria from the air must be remembered, although solutions of purified urea do not offer a medium favorable to microörganisms which can readily hydrolyze the urea in urine. To learn whether there were any secondary effects, the following experiment was carried out. The concentrations in the reacting mixture were 0.1 M urea, 0.01% urease preparation and 0.05% dl- α -alanine. No buffer was used and the ammonia could thus be determined by direct titration with alkali after the reaction had been stopped by the addition of standard sulfuric acid solution. To allow maximum opportunity for possible bacterial action and other effects the solutions described below were allowed to act for two days instead of for the usual time of two hours.

	TAB	E III	
Substances present besides distilled water	Cc. of 0.1069 I NH ₃ generated 10cc. sample	in present besides	Cc. of 0.1069 N NH; generated in 10cc, sample
Enzyme	0.0	Urea + α-alanine	(neutr.) 0.1
Urea	0.0	Urea + enzyme	3.1
α-Alanine (neutralized)	0.0	Urea + enzyme	+ α-alanine
Enzyme $+ \alpha$ -alanine (neutr.)	0.0	(neutr.)	

These results indicate that no ammonia is formed by hydrolytic or bacterial decomposition of urea, urease or α -alanine alone, or by interaction of the enzyme with the amino acid. Urea in the presence of α -alanine undergoes a small but measurable change, which may be due to a slight catalytic activity of the amino acid, or to bacterial action due to improvement of the medium for growth of microörganisms. In any case the effect could

⁸ Ford, J. Soc. Chem. Ind., 23, 414 (1904). Donath, Hofmeister's Beitr., 10, 390 (1907). Ref. 1i. Sherman and Walker, This Journal, 43, 2461 (1921). Sherman and Caldwell, ibid., 43, 2469 (1921); 44, 2923, 2926 (1922). Biedermann, Arch. Néerland. Physiol., 7, 151 (1922); through C. A., 17, 564 (1923).

⁹ Sherman and Naylor, This Journal, 44, 2957 (1922).

scarcely be observed in a two-hour reaction period and it is by no means an important part of the promoter effect reported in this paper. A similar experiment with histidine, in the presence of the phosphate buffer, confirmed the conclusion that there is only a negligible amount of ammonia formed by the action of the amino acid alone on urea. The α -alanine does not catalyze the hydrolysis of urea to an important extent but does increase the catalytic activity of the urease, and we are thus dealing with an undoubted promoter action.³

It is well known that aqueous solutions of enzymes lose their activity on standing at room temperature and that at higher temperatures this decomposition proceeds more rapidly. Our experiments showed that glycine in $0.001\,M$ concentration protected urease from heat destruction at $75\,^\circ$ to a marked degree. Experiments were then carried out to determine whether this protective action was great enough at room temperature to account for the promoter action reported in this paper. In one set of experiments the decomposition on standing in the absence of substrate of an aqueous solution of the enzyme alone and with an amino acid present was studied. In the other set of experiments the rate of decomposition of the enzyme with and without amino acid was determined in the presence of the substrate, that is, while the enzyme was functioning as a catalyst.

Decomposition in Absence of Substrate.—An experiment was conducted using the same procedure and the same concentrations as in the tests of the effect of added substances. As a control the activity of a freshly prepared enzyme solution was determined by a two-hour digestion after standing for 0 hours and 15 hours, respectively. The activity was also determined with amino acid present during digestion only, as well as with amino acid present during both periods. The results in cc. of 0.0653 N ammonia were as follows.

		Table IV	
Time of standing Hours	Control	dl-α-Alanine added just before digestion	dl-α-Alanine present both before and during digestion
0	4.73	5.45	5.39
15	3.25	3.67	3.87
% Decomp. in 15 hours	31	33	30

The decomposition of urease in presence of the amino acid was from 1 to 3% less than in the control over a 15-hour period, while the promoter action of the amino acid for a two-hour digestion was 14% with an enzyme solution tested immediately after dissolving the urease and 19% with an enzyme solution which had been standing 15 hours. Thus, while a slight protective action of the amino acid has been demonstrated, most of the increase in catalytic activity of the enzyme must be attributed to a direct promoter action.

Decomposition in Presence of Substrate.—When urease is added to a

solution of urea, and the amount of ammonia formed is determined for successive one-hour intervals, it is found that less urea is hydrolyzed during the second hour than during the first hour. This apparent decrease in rate of change may be ascribed to three causes: (1) to the decrease in concentration of substrate, (2) to a retarding effect of the products formed, and (3) to decomposition of the enzyme. Instead of expressing the experimental results in terms of the amount of ammonia formed in a given time, the length of time necessary to form a given quantity of ammonia may be obtained by interpolation on a curve in which the amount of ammonia formed is plotted against time. By this procedure the decrease in concentration of the substrate and any effects of the products formed will be the same in the control and in the parallel determinations, and the extent of decomposition of the enzyme may be closely estimated by comparing the percentage increase in time required in the two cases to bring about equal increments of change in successive intervals. That is, if in one digestion the enzyme is decomposing faster than in another, more time, proportionately, will be required for bringing about the second increment of change in the first case than in the second.

Experiments were carried out with dl- α -alanine and with histidine, using the same procedure and same concentrations as were used in the tests of the effect of various added substances.

Table V Expt. 125

				to form 1st	to form 2d
	Cc. of	0.0653 N NHs formed	in	3cc. of 0.0653 N NH ₂	3cc. of 0.0653 N NH2
	1 hr.	2 hrs.	3 hrs.	Min.	Min.
Control	2.63	4.84	6.72	70	88
dl - α -Alanine added	2.83	5.12	7.18	64	81

In the control the second period required 18 minutes longer than the first, indicating on the average 26% less enzyme activity during the second period. In the presence of dl- α -alanine 17 minutes longer was required, showing a 27% decrease in rate of enzyme action during the second period. These results show that the enzyme was being decomposed as rapidly in the presence of amino acid as when no amino acid has been added. Comparing the two first periods a decrease in time from 70 to 64 minutes or 9% was obtained by the addition of dl- α -alanine. Since

Table VI Expt. 126

	Cc. of 1 hr.	0.0653 N NH ₃ 2 hrs.	formed in 3 hrs.	Time required to form 1st 2.5 cc. of 0.0653 N NH ₂ Min,	Time required to form 2d 2.5 cc. of 0.0653 N NH Min,
Control	2.25	4.13	5.85	69	82
dl - α -Alanine added	2.40	4.49	6.31	62	75

the destruction of enzyme in each case was practically the same, the promoter action cannot be explained on the basis of a prevention of destruction of the enzyme.

Thirteen minutes longer was required for the second period in each case, indicating on the average a 19% slower rate of action in the control and a 21% slower rate of action in the presence of dl- α -alanine during the second period. These results indicate that the enzyme is destroyed as rapidly while exerting its catalytic effect in the presence of dl- α -alanine as in its absence. The amino acid brought about a 10% decrease in time required for the first period (as is seen by comparing the two first periods), and this promoter action, is, therefore, due to an increased activity of the enzyme brought about by the amino acid.

The results obtained with histidine led to the same conclusion as those with dl- α -alanine. The experiments thus disprove the hypothesis that the promoter effect is due chiefly to prevention of decomposition of the enzyme. On the other hand, the results support the view that the promoters directly facilitate the interaction of the enzyme with the substrate.

Summary

- 1. It has been found that certain compounds exert a promoter effect on the catalytic activity of the urease of the jack bean. It was also shown that some compounds have an inhibitory action. These effects are independent of changes in hydrogen-ion concentration and do not result from the attainment of a concentration of electrolytes more favorable or unfavorable to the action of the enzyme.
- 2. The promoter effect is related to the presence of amino and carboxyl groups in the same compound, since each promoter contained both these groups, while compounds containing only one of them were not promoters.
- 3. The results with both aliphatic and aromatic compounds containing an amino and a carboxyl group indicate that the promoter action is a function of the distance between these groups, the stimulating effect increasing with decrease in their proximity. All α -amino acids tested are marked promoters, β -amino acids have a slight promoter action, and γ -amino acids have no effect. The isomeric aminobenzoic acids, in order of decreasing promoter effect are: ortho > meta > para.
- 4. In α -amino acids, replacement of one hydrogen of the amino group by benzoyl, or esterification of the carboxyl group does not diminish the promoter action.
- 5. A second carboxyl group in an α -amino acid appears to increase the promoter effect slightly.
- 6. A second amino-group in an α -amino acid was found to increase the promoter action.

- 7. A second amino group in a compound already containing one amino and two carboxyl groups, or a second carboxyl group in a compound already containing one carboxyl and two amino groups does not appear to increase the promoter effect.
- 8. α -Amino acids with a nitrogenous heterocycle give, on the average, a somewhat greater promoter effect than simple α -amino acids.
- 9. There is some indication that in aliphatic α -amino acids the promoter effect decreases with lengthening carbon chain.
 - 10. In α -amino acids, optical isomers do not differ in promoter effect.
- 11. Ammonium chloride has no promoter action when changes in hydrogen-ion concentration are eliminated and correction is made for the ammonia it contains. Thus the favorable effect of ammonium chloride reported by others^{1a} is not the specific effect demonstrated in this investigation.
- 12. From the results of our work it appears that the effect of a compound on the activity of urease may furnish valuable presumptive evidence as to the presence of an amino group in the α position to carboxyl.
- 13. The experiments which show the promoter action of α -aminocarboxylic acids and of peptones indicate that the protein part of enzyme preparations is an important factor in the action of the enzyme because its promoter action accounts for part of the activity of the enzyme.
- 14. The experiments tend to disprove the hypothesis that the promoter effect is due chiefly to prevention of decomposition of the enzyme. On the other hand, the results support the view that the promoters directly facilitate the interaction of the enzyme with the substrate.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A NEW METHOD FOR THE DETERMINATION OF ACETIC ACID IN ACETIC ANHYDRIDE

By James H. Walton and Lloyd L. Withrow Received July 23, 1923

Acetic anhydride has become so important a reagent in organic synthesis, that a rapid and accurate method for determining its chief impurity, acetic acid, is very desirable. In a recent investigation by E. R. Schierz¹ and the senior author of this paper a method for determining this substance was indicated.

When formic acid is added to acetic anhydride, it is broken up quantitatively according to the equation $HCOOH = H_2O + CO$. At ordinary temperatures the reaction proceeds so slowly that it is practically unmeasurable. It was found by Schierz that this reaction is catalyzed by

¹ Schierz, This Journal, 45, 455 (1923).

the following tertiary nitrogen bases which are listed in the order of decreasing activity: strychnine, brucine, nicotine, cocaine, pyridine, morphine, quinine.

In the presence of small amounts of acetic acid the catalytic activity of certain of these compounds was greatly reduced. Since the retardation was found to be proportional to the concentration of the acetic acid it was thought that this effect could be used as the basis of a method for determining small amounts of acetic acid in acetic anhydride. It was planned to prepare pure acetic anhydride and measure the rate of decomposition in the presence of a given concentration of catalyst. The rate of decomposition in the presence of various concentrations of acetic acid could then be determined, and these data used to plot a curve showing the effect of acetic acid on the catalytic decomposition of formic acid. A solution of acetic anhydride could then be analyzed by adding the proper amounts of formic acid and catalyst, measuring the velocity of decomposition and reading on the curve the percentage of acetic acid corresponding to the velocity constant obtained.

Acetic Anhydride.—A commercial preparation labeled 97% was used for the preparation of the pure anhydride. To remove the acetic acid this material was allowed to stand in contact with thin slices of metallic sodium for several days. The mixture was then refluxed under reduced pressure for several hours and was finally distilled from a mixture of metallic sodium and sodium acetate. The latter substance aids in the retention of any free acetic acid that might still be present. On distilling the acetic anhydride the first portion that came over was greenish. This was discarded. The latter portion distilled at a constant temperature. Its physical constants, stated below, compare favorably with those given by Orton and Jones: b. p., 139.3 (740 mm.); d^{26} , 1.0765; n_D^{25} , 1.3885; n_D^{31} , 1.3863. Further evidence of the purity of this anhydride is the fact that when frozen in liquid air it congealed without clouding. When anhydride of 98.7% purity was frozen, crystals of acetic acid separated at -50° . The anhydride prepared by the method described above melted at -86° .

This anhydride was tested for the presence of acetaldehyde by the method of Stepp and Frick. Approximately 0.1% was found present. Acetone was absent.

Strychnine.—Commercially pure strychnine was recrystallized from ethyl alcohol and dried at 100°.

Formic Acid.—An 85% solution was dehydrated at 50° with anhydrous oxalic acid. The solution was then cooled and the crystals of oxalic acid were filtered off. Upon distillation a very concentrated solution was obtained. This was dehydrated with boric acid and distilled, a product practically 100% pure being obtained.

Apparatus.—The velocity of decomposition of the formic acid was determined by placing the reaction mixture in a flask containing some pieces of glass rod, shaking it vigorously to avoid supersaturation, and measuring the rate of evolution of gas by collecting it over water in water-jacketed burets.⁵ The catalyst and anhydride were first placed in the flask. The formic acid was placed in a capsule held in the neck of the flask

² Orton and Jones, J. Chem. Soc., 101, 1720 (1912).

³ Stepp and Frick, Z. physik. Chem., 116, 233 (1921).

Schlesinger and Martin, This Journal, 36, 1589 (1914).

Walton, Z. physik. Chem., 47, 185 (1904).

in such a manner that it could be dropped whenever desired. The reaction takes place very slowly at room temperature, so all determinations were made at 35°. It was shown by Schierz that this reaction is monomolecular.

Results.—Table I summarizes a typical run made with the pure anhydride, formic acid and catalyst. In this experiment, as in all others made in this investigation, 25 cc. of acetic anhydride, 0.25 g. of strychnine (catalyst) and 0.07 cc. of formic acid were used in each experiment. This amount of formic acid gives about 35 cc. of carbon monoxide measured at 0° and 760 mm. In this table, T, X, A and K have their usual significance in the formula for a reaction of the first order.

TABLE I
THE DECOMPOSITION OF FORMIC ACID IN PURE ACETIC ANHYDRIDE USING STRYCHNINE
AS CATALYST

T	X	A - X		K
1.5	18	19.8	•	0.437
2	22.3	15.7		.440
2.5	25.8	12.2		.452
3	28.2	9.8		.450
3.5	29.2	8.8		.421
4	31.8	7.2		.415
5	34	4.0		.436
A = 38.00			Av.	.434

Repeated: K = 0.425 and 0.487

It will be noted that this experiment was extremely rapid, the reaction being almost 90% complete in 5 minutes. Taking this fact into consideration, the agreement of the constants is satisfactory. The acetic anhydride used in each of the experiments was purified and freshly distilled for that particular experiment. It is believed that no one of these samples contained more than a slight trace of acetic acid.

Since the acetic anhydride contains a small amount of aldehyde the influence of the presence of this substance on the rate of the reaction was investigated. When present to the extent of 5% in a sample of acetic anhydride containing a small quantity of acetic acid it changed the velocity constant from 0.320 to 0.315; the effect can consequently be neglected. Schierz showed that the rate of the reaction is not influenced by the presence of small quantities of ketones or aromatic aldehydes.

A number of experiments were carried out to determine the effect of various concentrations of acetic acid on the velocity of this reaction. Since the rate of decomposition in the presence of acetic acid is slower, more concordant results than those listed in Table I were obtained. Because of the extreme slowness of the reaction, concentrations of acetic acid greater than 5% were not used. The results of the experiments are given in Table II and are shown graphically in Fig. 1.

These results indicate that wherever the analysis of acetic anhydride for acetic acid is a part of the routine work this method will be found satisfactory. It is extremely rapid and sufficiently accurate for most purposes. For determining the presence of very small amounts of acetic acid the method can be improved by carrying out the experiment at 25°;

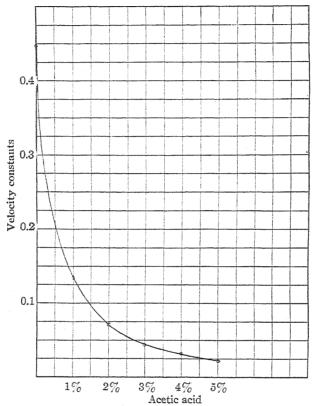


Fig. 1.—The influence of acetic acid on the catalytic decomposition of formic acid

at this temperature the reaction would be almost half as fast and the velocity could be measured more accurately. For higher concentrations of acetic acid than 5% a temperature of decomposition higher than 35°

TABLE II

THE EFFECT OF ACETIC ACID UPON THE RATE OF DECOMPOSITION OF FORMIC ACID IN

ACETIC ANHYDRIDE SOLUTION

Conen, of acid	K	$K_{ ext{dup}}$.	Kav.	K conen. acid				
0			0.447	•••				
1	0.134	0.135	0.135	0.135				
2	.0664	.0689	.677	.135				
3	.0468	.0467	.468	.140				
4	.0334	.0319	.327	.130				
5	.0236	.0238	.237	.119				

could be used or the solution diluted with enough pure acetic anhydride to bring the concentration of the acetic acid to approximately 5%.

The last column of Table II shows that when from 1 to 4% of acetic acid is present the value [Velocity constant \times concn. acetic acid] equals a constant. In other words the retardation of this reaction is directly proportional to the concentration of acetic acid. When more acetic acid is added this relationship does not hold.

Summary

- 1. A method for preparing acetic anhydride of a high degree of purity is described and certain physical properties of the anhydride have been determined
- 2. The effect of different concentrations of acetic acid upon the rate of decomposition of formic acid in acetic anhydride solution, using strychnine as a catalyst, has been determined. This forms a basis for the quantitative analysis of acetic anhydride for acetic acid when 1 to 5% of this impurity is present.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]
STUDIES CONCERNING THE DIRECT PREPARATION OF
ORGANOBERYLLIUM HALIDES1

By Henry Gilman Received July 31, 1923

Introduction

Much of the importance of organometallic compounds in synthetic work is confined to those compounds formed from metals of the second group of the periodic system. Zeltner,² from a study of many organometallic compounds, has called attention to two apparently general rules concerning the reactivity of such compounds which have each of the ordinary valences of the metal satisfied by an alkyl or aryl group. First, in a given group of metals having the same radicals attached to the metal, that organometallic compound with the metal of lowest atomic weight is most reactive. Second, with a given metal, that organometallic compound which has the lightest radicals is most reactive.

If these generalizations are true, it follows that one should expect an organoberyllium compound having alkyl groups of low molecular weight to be most reactive in a group which already contains several organometallic types of high reactivity. If organoberyllium halides could be prepared and if they should exhibit this reactivity, they might make pos-

¹ An abstract of a paper presented at the Intersectional Meeting of the American Chemical Society held at Urbana, Illinois, May 5, 1923.

² Zeltner, J. prakt. Chem., 77, 393 (1908).

sible a number of reactions which cannot be realized with the ordinary Grignard reagent of the general formula RMgX.

The organometallic halides or "mixed organometallic compounds," largely because of their ease of preparation, convenience in handling, and high reactivity, have displaced almost completely from synthetic work the longer known, simple organometallic compounds which have no halogen directly attached to the metal.

Simple organoberyllium compounds such as beryllium diethyl and dipropyl have long been known.³ No mention, however, is to be found in the literature of an organoberyllium halide. Several investigators have attempted to prepare such compounds directly. Grignard⁴ tried without success to bring metallic beryllium into reaction with a simple alkyl halide. Simonis⁴ tried methyl iodide, bromobenzene, and benzyl bromide in absolute ether, using iodine as a catalyst, but could get no one of the compounds to react with his beryllium. Kamm⁴ tried methyl iodide, ethyl iodide and ethyl bromide and, using freshly prepared Grignard reagent as a catalyst, likewise failed to bring about a reaction.

The following series of unsuccessful attempts was made to prepare organoberyllium halides.

Experimental Part

The metallic beryllium used was obtained from five different sources. Two samples came from foreign manufacturers, a third from Dr. Simonis of the Charlottenburg Technische Hochschule who sent a sample of the beryllium he had used, a fourth from Dr. Hopkins of the University of Illinois, and a fifth from Dr. Stock of the Kaiser Wilhelm-Institut. Although all samples have been shown by analysis to contain at least 98% of beryllium, that provided by Dr. Stock is claimed to be the purest beryllium for which letters patent have been issued; it has been shown by analysis to contain more than 99% of beryllium.

All of the other chemicals used, particularly the ether and other solvents and the various alkyl and aryl halides, were prepared freshly in a very high state of purity. The apparatus was periodically tested in the sense that Grignard reagents were readily prepared in it, using both magnesium turnings and powder, various halides and various solvents.

The factors varied in the many studies were the halides, solvents, temperature, time of heating, and catalysts. The halides used were methyl iodide, ethyl iodide, benzyl bromide, bromobenzene, chlorobenzene and α -bromonaphthalene. In addition to the commonly used solvent, anhydrous ether, anisole, benzene and β -ethoxy-naphthalene were tried. Using the bromonaphthalene and ethoxy-naphthalene, the temperature of

³ Cahours, Compt. rend., 76, 1383 (1873).

⁴ Private communication.

U. S. pat., 1,427,919, Sept. 5, 1922.

one series of experiments was as high as 245–250°. The time allowed for some runs was as much as two weeks, and in the shorter runs, all of which extended over 12 hours, the material was stirred almost continuously. Conventional catalysts such as iodine, bromine, dimethyl aniline, freshly prepared Grignard reagent (sometimes directly prepared in the reaction mixture) were used repeatedly. Ethyl acetate, which is so useful in the preparation of organozinc iodides, was tried as a catalyst in one experiment.

In some experiments sublimed beryllium iodide, freshly prepared in a vacuum by subliming iodine onto heated beryllium, was used. Also, to overcome the objection that the metal might be coated with an oxide, it was shaken before use in one experiment with very dilute, pure nitric acid, and then while gas evolution continued was quickly filtered, washed, dried and used directly. In one experiment the reaction mixture was exposed to X-rays.⁶

As a final proof that conditions were as nearly satisfactory as possible for a reaction, some magnesium was added at the end of every experiment, either to a part or the whole of the reaction mixture, and in every case a reaction took place between the magnesium and halide.⁷

In no experiment was there any evidence of a reaction between the beryllium and halide.

Conclusion

The experiments outlined are sufficiently general to indicate that metallic beryllium does not enter directly into reaction with halides to form organo-beryllium halides. There are, however, several methods for the indirect preparation of organoberyllium halides, and a study is being made of such reactions.

The author wishes to acknowledge gratefully the kindness of Doctors Grignard, Simonis, Stock, Kamm, and Hopkins for the help they have given in supplying some of the metal used, and for the unpublished accounts of their work.

Summary

A series of unsuccessful attempts has been made to bring metallic beryllium into reaction with a variety of halides in an effort to prepare organoberyllium halides.

AMES, IOWA

⁶ Work done by Mr. B. Toubes.

⁷ In connection with another study, the results of which will be published shortly, a detailed account will be given of a general test for some organometallic halides.

[Contribution from the Chemical Laboratory of the University of Illinois]

IDENTIFICATION OF AMINES

By C. S. Marvel and F. E. Smith Received August 1, 1923

Many crystalline products are available for the identification of primary and secondary amines since most of their acetyl, benzoyl and benzene-sulfonyl derivatives are known solids. However, certain of these derivatives are not entirely satisfactory because their melting points lie too close to one another.

Benzenesulfonyl chloride has been shown¹ to be a particularly desirable reagent in the examination of amines and is almost always used in routine qualitative organic analysis of nitrogen compounds. However, some of the benzenesulfonyl derivatives of the commoner amines are oils or low-melting solids, and after application of the Hinsberg test, another solid derivative must be prepared for complete identification.

Ssolonina² has prepared the p-bromobenzenesulfonyl derivatives of a few amines and has found that as a rule these melt higher than the unbrominated compound. It was thought that p-bromobenzenesulfonyl chloride would be useful to replace benzenesulfonyl chloride in the Hinsberg test, as better melting substances could be expected.

The p-bromobenzenesulfonyl amides of most of the common amines have now been prepared and characterized. As a general rule they are easily crystallizable compounds with sharp melting points. They make especially good derivatives for ethyl aniline, n-propylaniline, n-butyl-aniline and piperidine. However, p-bromobenzenesulfonyl chloride cannot be used in place of benzenesulfonyl chloride in the Hinsberg test because it gives alkali insoluble derivatives with many primary amines. This insolubility may be explained by the theory developed by Adams³ to explain the alkali insolubility of certain phenols.

Experimental Part

p-Bromobenzenesulfonyl Chloride.⁴—This reagent is readily obtained by heating a mixture of 100 g. of sodium p-bromobenzenesulfonate and 70 g. of phosphorus pentachloride on the water-bath for about 16 hours. After the mixture has cooled, water is added to destroy the phosphorus oxychloride and the p-bromobenzenesulfonyl chloride which separates is filtered and washed with water. After the product is carefully washed it is dried. The yield is 85 to 90 g. (86–90%) of a product melting at 75°. The reagent may be recrystallized from petroleum ether if a very pure product is desired.

- ¹ Hinsberg, Ber., 23, 2963 (1890).
- ² Ssolonina, Chem. Zentr., [2] 1899, 867.
- ³ Adams, This Journal, 41, 247 (1919).
- ⁴ Ann., 180, 98 (1876).

Preparation of the p-Bromobenzenesulfonamides.—p-Bromobenzenesulfonyl chloride is treated with a slight excess of the amine and warmed if necessary to start the reaction. The reaction takes place smoothly with the evolution of heat and after a few minutes is complete. The excess amine is removed by washing the product with dil. hydrochloric acid. The crude product is then recrystallized from alcohol of the proper strength, depending on the particular compound used (see Table I).

The derivatives of methylamine, dimethylamine and piperidine are prepared by treating a water solution of the amine hydrochloride with p-bromobenzenesulfonyl chloride and aqueous alkali in the usual manner.

The new compounds that have been prepared are given in Table I, together with their physical properties and analyses.

Diethylamine gives an oily product which solidifies in an ice-bath. Since it is not of use as a derivative it was not analyzed.

Table I Para-Bromobenzenesulfonamides

	ر پ		of sed	Sure C.	Analy	sis		
	of t °	ant P.	th th	. <u> </u>	<u>ن</u>	nd		lubility i
Amine	rudge duct	constar m. p	hol	p. of poduct	calc.	found %	10	% NaOl solution
	M. p. crude product No. of cryst. to	ပိ	Strength alcohol us	m cryst. M. p. of product	Ä	Br		501411014
Methylamine	75 - 77	2	92	77	32.0	31.9		+
Benzylamine	115	1	60	117	24.5			+
Dimethylamine	93	1	60	94	30.3	29.7		· . · -
Piperidine	88	1	92	91	26.3	26.1		
o-Toluidine	92-104	3	80	116	24.5	24.9		-
p-Toluidine	96-97	2	92	98	24.5	24.6		
o-Chloro-aniline	103	1	60	105^{d}	28.8^{a}	28.8^{a}		
p-Chloro-aniline	130-132	1	60	134^e	29.2^{b}	29.2^{b}		
p-Bromo-aniline	121-126	3	92	145^e	40.9	40.7		
p-Anisidine	120-125	2	92	142	23.4	23.3		+
p-Phenetidine	135-140	2	92	143	22.7	23.8		+
α-Naphthylamine	158-167	2	92	183.5	22.1	22.2		
β -Naphthylamine	125-128	2	80	129	22.1	22.4		
Monomethylaniline	88	2	80	92	24.5	23.6		-
Mono-ethylaniline	82-85	2	92	91	23.5	23.6		_
Monopropylaniline	95-102	3	60	109	22.6	22.4		_
Monobutylaniline	81-86	2	60	87	21.7	21.8		. – ::
p-Bromo-ethylaniline	117	1	60	118.5	38.2	38.0		_

^a Cc. of 0.1001 N AgNO₃ required for the halogen and not % of Br.

^b Cc. of 0.0981 N AgNO₃ required for the halogen and not % of Br.

^o p-Bromo-ethylaniline was prepared in connection with another problem by brominating ethylaniline in glacial acetic acid. The compound boils at 143–147° at 20 mm. Calc. for C₈H₁₀ NBr:Br, 40.0 Found: 39.61.

^d Slightly soluble in hot NaOH; insoluble in cold.

Soluble in hot NaOH; slightly soluble in cold.

Summary

The p-bromobenzenesulfonyl derivatives of several common amines have been characterized. These compounds are useful for the identification of amines.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE ALLYL ETHERS OF VARIOUS CARBOHYDRATES

By C. G. Tomecko1 with Roger Adams

RECEIVED AUGUST 3, 1923

Some of the most important developments in the chemistry of carbohydrates during the past fifteen years have been through the use of the alkyl ether derivatives. The original method of alkylation, as developed by Irvine² and his co-workers, was by means of silver oxide and alkyl iodides. More recently, an improvement has been made upon this procedure by Haworth3 who has used methyl and ethyl sulfates in place of the alkyl iodides; with these reagents aqueous alkaline solutions or suspensions are employed and the preparation of the ethers is thus rendered very simple. Of especial interest may be mentioned that the ethers of the disaccharides have been used in the determination of the structure of the disaccharides; the ethers of cellulose apparently are of commercial importance and consequently their preparation by this same process has engaged the attention of many investigators. In spite of the general interest and importance of the ethers of the carbohydrates, no other ethers than the methyl and ethyl derivatives have been prepared until very recently. Gomberg and Buchler4 made the benzyl derivatives of a variety of carbohydrates, following the same procedure as with the alkyl sulfates: this was possible due to the great reactivity of the chlorine in the benzyl chloride. In that paper a review of the previous articles discussing alkylation was given. Since that time many patents⁵ have appeared on the

- ¹ This communication is an abstract of a portion of a thesis submitted by C. G. Tomecko in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.
 - ² Purdie and Irvine, J. Chem. Soc., 83, 1021 (1903).
 - 3 Haworth, ibid., 107, 8 (1915).
- ⁴ Gomberg and Buchler, This Journal, **43**, 1904 (1921). See also U. S. pat., 1,451,331; C. A., 17, 2505 (1923).
- Lilienfeld, Brit. pat. 163,016, 163,017, 163,018 [C. A., 15, 3207 (1921)]; Can. pat. 220,831 [C. A., 16, 2989 (1922)]; Brit. pat. 177,810 [C. A., 16, 3206 (1922)]; Brit. pat. 181,392, 181,393, 181,395 [C. A., 16, 3758 (1922)]; Can. pat. 222,377 [C. A., 16, 4087 (1922)]; U. S. pat. 1,441,889 [C. A., 17, 1141 (1923)]. Young, Brit. pat. 184,825 [C. A., 17, 878 (1923)]. Clancy, U. S. pat. 1,439,293 [C. A., 17, 879 (1923)]. Seel, U. S. pat. 1,437,820, 1,437,821 [C. A., 17, 879 (1923)]. Dreyfuss, Brit. pat. 187,639 [C. A., 17, 1141 (1923)].

methylation and ethylation of cellulose, as well as numerous scientific papers involving the methylation of or ethylation of a variety of different carbohydrates.

From a practical standpoint the methyl and ethyl ethers are at present the only types which are of particular interest, but from a theoretical standpoint the preparation and study of other types of ethers should lead to important results. An investigation was undertaken in this Laboratory to prepare such ethers of the carbohydrates as contain in the ether groups other active groups through which new types of carbohydrate compounds may be prepared and studied. Such new ethers may be formed by allowing active halogen compounds to react with an alkaline solution or suspension of the carbohydrate; of these may be mentioned the first two that have been studied, allyl bromide and chloro-acetic acid.

This preliminary communication describes work on the allylation of carbohydrates with allyl bromide and sodium hydroxide. Owing to the great reactivity of the bromine, the introduction of the allyl group is extremely simple and good yields of products are obtained. The number of ether groups introduced corresponds to the number of benzyl groups introduced by benzyl chloride and sodium hydroxide.

The products resemble in physical properties the corresponding methyl and ethyl derivatives. The tetra-allyl- α -methyl glucoside is a highboiling, viscous liquid that can be distilled under diminished pressure without decomposition. Penta-allyl sucrose is a viscous oil that cannot be distilled without decomposition. Mono-allyl inulin, mono-allyl potato starch, mono-allyl corn starch, mono-allyl dextrin and allylated cellulose are practically white, amorphous substances that were purified by solution in various organic solvents and then reprecipitation with ether. They give rather indefinite decomposition points. Various derivatives of the new allyl ethers are now being studied.

No record of the preparation of allyl ethers of carbohydrates has previously appeared. The only allyl derivatives of the carbohydrates which have been mentioned are the allyl glucosides prepared by Fischer⁷ and Bourquelot.⁸

Experimental Part

One molecular equivalent of carbohydrate was dissolved or suspended in 10% sodium hydroxide containing an excess of alkali (2 to 2.5 mo-

⁶ Denham and Woodhouse, J. Chem. Soc., 119, 77 (1921). Karrer and Nagelli, Helvetica Chim. Acta, 4, 185 (1921). Karrer and Lang, ibid., 4, 249 (1921). Irvine, Steele and Shannon, J. Chem. Soc., 121, 1060 (1922). Irvine and Hirst, ibid., 121, 1213 (1922). Irvine and Patterson, ibid., 121, 2696 (1922). Heuser and Neunstein, Cellulosechemie, 3, 101 (1922). Haworth and Linnell, J. Chem. Soc., 123, 294 (1923). Haworth and Mitchell, ibid., 123, 301 (1923). Irvine and Hirst, ibid., 123, 518 (1923).

⁷ Fischer, Ber., 45, 2467 (1912).

⁸ Bourquelot, Compt. rend., 155, 437 (1912); 156, 1493 (1913).

A SAMPARA

lecular equivalents). This mixture was heated on a water-bath and stirred mechanically while an excess of allyl bromide was dropped in slowly. It was generally advisable to heat the reaction mixture on a water-bath for about an hour after all the bromide had been added. The reaction mixture was then steam distilled to remove any allyl alcohol or excess of allyl bromide, the oily or gummy reaction product washed with water and purified. The yields, properties and methods of purification are described under the individual substances.

All analyses were made on the solids after drying in a vacuum at 110° for 24 hours. It was found that two or three of the allylated compounds did not give analyses as close to the calculated values as might be expected. In these cases duplicate analyses were carried out on subsequent reprecipitations and in every instance gave check results with those analyses which are reported. This led to the conclusion that certain of the mono-allyl derivatives were contaminated, perhaps with small amounts of higher allylated compounds which had very similar properties to the mono-allyl derivatives and were not removed by the precipitations.

None of the solids prepared had a definite melting or decomposition point. Since melting points were reported for the benzylated compounds⁴ two or three of these were made in this Laboratory and the effect of temperature determined. The points mentioned by these authors as melting points are unquestionably points of decomposition resembling closely the type of decomposition found for the allylated compounds. The "melting points" reported for the benzyl compounds are actually the points where the various materials start to shrink.

Tetra-allyl- α -methyl Glucoside.—From 100 g. of α -methyl glucoside, 249 g. of allyl bromide and 124 g. of sodium hydroxide, there was obtained 83 g. of purified tetra-allyl- α -methyl glucoside boiling at 182° (1.5 mm.); $n_{\rm D}^{18}$, 1.4836; d_{20}^{20} , 1.1519; $[\alpha]_{\rm D}^{30}$, 116.5° (in absolute alcohol). It is a thick, colorless oil, insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.1503: CO_2 , 0.3160; H_2O , 0.1070, Calc. for $C_{19}H_{30}O_4$: C, 64.41, H, 8.47. Found: C, 64.13; H, 7.93.

Penta-allyl Sucrose.—From 100 g. of sucrose, 340 g. of allyl bromide and 141 g. of sodium hydroxide there was produced 118 g. of the penta-allyl derivative. The crude reaction product was taken up in chloroform, filtered and the chloroform evaporated. There was thus formed a practically colorless, thick oil which could not be distilled under diminished pressure without decomposition. It was insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.4710: CO₂, 1.0232; H_2O , 0.3056. Calc. for $C_{27}H_{42}O_{11}$: C, 59.59; H, 7.74. Found: C, 59.21; H, 7.58.

Mono-allyl Dextrin.—From 25 g. of dextrin, 100 g. of allyl bromide and 75 g. of sodium hydroxide there was obtained 16 g. of allylated dextrin. The crude product formed a gummy mass. This was purified by dissolving it in chloroform and precipitating with ether. After a number of such treatments a practically white, amorphous solid was obtained, shrinking at 155–165° and gradually decomposing at about 240–250°.

Analyses. Subs., 0.3876: CO_2 , 0.7334; H_2O , 0.2260. Calc. for $C_{18}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 51.41; H, 6.43.

Mono-allyl Inulin.—From 10 g. of inulin, 100 g. of allyl bromide and 75 g. of sodium hydroxide there was obtained about 5 g. of gummy product. When this was treated with a limited amount of cold alcohol, it dissolved and was then reprecipitated with ether. Care must be taken not to add too much alcohol as such an excess also causes precipitation. Further purification was effected by dissolving the material in glacial acetic acid and reprecipitating it with ether. There was thus produced 3 g. of nearly white product, shrinking at 150–155° and decomposing at 205–210°.

Analyses. Subs., 0.3014: CO_2 , 0.5330; H_2O , 0.1898. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 48.22; H, 7.00.

Mono-allyl Potato Starch.—From 10 g. of potato starch, 85 g. of allyl bromide and 50 g. of potassium hydroxide, a gummy product was produced. This was dissolved in alcohol as described under allyl inulin and reprecipitated with ether, then twice dissolved in glacial acetic acid and reprecipitated with ether. The final product was practically white and weighed 10 g. It shrank at 160–165° and decomposed without melting at about 260–270°.

Analyses. Subs., 0.3470: CO₂, 0.6318; H_2O , 0.2054. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 49.64, H, 6.55.

Mono-allyl Corn Starch.—From 10 g. of corn starch, 110 g. of allyl bromide and 75 g. of potassium hydroxide there was obtained a gummy product which was purified like the mono-allyl potato starch. A practically white, amorphous product resulted which weighed 12 g. It became brown at about 250–265 $^{\circ}$ but did not shrink or melt.

Analyses. Subs., 0.3447: CO₂, 0.5699; H_2O , 0.1853. Calc. for $C_{18}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 50.41; H, 6.70.

Allylated Cellulose.—Pure filter paper was hydrated by dissolving it in cuprammonium hydroxide and precipitating in the usual way. From 10 g. of this precipitated cellulose, 85 g. of allyl bromide and 65 g. of potassium hydroxide there was obtained a residue which was treated with several portions of cuprammonium hydroxide. The material that remained undissolved was carefully dried and analyzed.

Analyses. Subs., 0.3852: CO₂, 0.6313; H_2O , 0.2211. Calc. for $C_{15}H_{24}O_{10}$: C, 49.44; H, 6.59. Found: C, 45.15; H, 6.44.

The product was obviously impure as shown by the analysis, but this was unquestionably due to the fact that no solvent for crystallization was found.

Summary

Several different types of carbohydrates have been treated in aqueous alkaline solution or suspension with allyl bromide. Under these conditions allyl derivatives of these carbohydrates are produced.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VALE UNIVERSITY]

STUDIES ON CATALYSIS. III. THE REDUCTION OF URACIL TO HYDRO-URACIL

By Elmer B. Brown and Treat B. Johnson Received August 6, 1923

In a preliminary paper ^{1a} the writers have reported a new method of reducing the pyrimidine, uracil (I). They have applied Skita's method of catalytic reduction and have shown that this substance is reduced quantitatively with hydrogen to hydro-uracil (II) in the presence of colloidal platinum or palladium. In this paper, which is a report of their experimental work on this compound, the writers have extended their study of this catalytic reduction process, using uracil in order to establish the limiting conditions under which the reduction process in the presence of colloidal platinum or palladium can be carried out when applied to the

pyrimidine series. In the experimental part of the paper are recorded the results of our experiments showing the influence on the progress of the reduction of different foreign substances that are commonly met as impurities in the naturally occurring products containing the pyrimidines, thymine, cytosine and uracil. Sulfur compounds, which are of very common occurrence in nature and are often found as impurities in the solutions obtained in the isolation of the pyrimidines from that source, as well as in our synthetic methods of preparation, are shown to prevent reduction completely when present even in traces. The effect of the presence of thiopyrimidines and other sulfur combinations on the reduction process is similar to the results obtained by Willstätter and Hatt,² who found that traces of thiophene, for example, completely stopped the hydrogenation of benzene when platinum black was used as catalyst. The chlorides of sodium, potassium, calcium and magnesium exert no influence upon the reduction process in the case of uracil.

The reduction of uracil to hydro-uracil proceeds quantitatively when carried out under the conditions described in this paper and, so far as the writers are aware, no other method of bringing about this change successfully is available. Electrolytic reduction methods have been applied with success in the barbituric acid series, and hydro-uracil has been prepared, for example, by electrolytic reduction in acid solution of several

¹ Previous publications: (a) Johnson and Brown, *Proc. Nat. Acad. Sci.*, 7, 75 (1921); (b) Gilfillan, This Journal, 44, 1323 (1922).

² Willstätter and Hatt, Ber., 45, 1471 (1912).

pyrimidines, namely, barbituric acid, dialuric acid, uramil and alloxan, but secondary products were always formed in these operations, and the yield of hydro-uracil was generally very low.3 In fact, it has been shown that hydro-uracil can be reduced still further with formation of trimethylene-urea. The reduction of uracil to this substance can probably be accomplished by our method but apparently with great difficulty only, and at present conditions have not been established whereby it has been possible to obtain this cycle in satisfactory yields for synthetic work. The fact that uracil can be reduced so easily to hydro-uracil is of special interest to us from a biochemical point of view. If the catalytic method of reduction can be shown to be one of general application in the uracil series we will have opened up a method of synthesizing β -amino acids which will prove of great practical interest. These reduced pyrimidines bear a similar relationship to β -amino acids that the hydantoins do to α -amino acids, and on hydrolysis with acids or bases are susceptible to the same hydrolytic change. This relationship is revealed by examination of the following equations.

NH—CO
$$\rightarrow$$
 NH₂ COOH \rightarrow NH₂ COOH \rightarrow NH₃ + CO₂ + NH₂CH(R)COOH (1) NH—CHR \rightarrow NH—CHR \rightarrow NH—CHR \rightarrow NH—CHR \rightarrow NH—CHR \rightarrow NH—CO \rightarrow NH₂ COOH \rightarrow CO \rightarrow NH₂ COOH \rightarrow CO \rightarrow NH₂ COOH \rightarrow NH—CH₂ \rightarrow NH₂ \rightarrow N

Process 2 offers greater possibilities for amino acid synthesis than the hydantoin method which has been developed so extensively in the Yale Laboratories, because two carbon atoms are available to which substituent groups or radicals may be attached. Having available the proper uracil derivative, and an easy practical method of reduction at the double

bond in Positions 3 and 4, it will be possible to synthesize by our method several β -amino acids which are unknown, and are not easily obtained by the present methods of synthesis at our command. This investigation is being continued in the Sterling Chemistry Laboratory.

Experimental Part

Purification of Uracil.—The pyrimidine used in this research was prepared by students in the laboratory by application of the thio-urea method and was of a fair degree

³ Tafel and Weinschank, Ber., 33, 3385 (1900). Tafel and Reindl, ibid., 34, 3286 (1901).

of purity, although not of sufficient purity to permit its use in our catalytic reduction work. One hundred g. of uracil was repeatedly recrystallized from water, using Norite to remove all coloring material, when a product was easily obtained which failed to respond to the sulfur test and was apparently free from this impurity. However, in order to remove the minutest trace of sulfur impurities, 50 g. of the product described above was further purified by refluxing for 3 hours with a 2% solution of monochloro-acetic acid and then recrystallizing twice from water. In this manner we obtained a colorless sulfur-free product which caused no difficulty in our reduction operations.

The Reduction of Uracil to Hydro-uracil.—Six g. of pure uracil is placed in the reduction flask, and to this 2 g. of gum arabic dissolved in 50 cc. of hot water, 10 cc. of 10% chloroplatinic acid solution and 150 cc. of water is added. The reduction flask is then placed in position in an electric heater on a shaking machine and connected with a cylinder of hydrogen. After removal of the air from the reduction flask hydrogen is introduced until a pressure of two atmospheres is obtained, the shaking machine is then started and the electric current turned on. Within a short time the solution turns black and there is very rapid absorption of hydrogen and the formation of colloidal platinum. The temperature is soon increased to 75°, and maintained at that point by proper regulation of the electric current. The calculated amount of hydrogen is absorbed in 5 to 7 hours, and the absorption ceases under the above conditions when one molecular equivalent of hydrogen has been taken up.

The reduction solution is now poured into an equal volume of acetone and the precipitated colloid allowed to settle. Usually one hour suffices for complete separation of the colloid, leaving a clear solution which is easily filtered. The acetone is distilled and can be used for the same purpose again without further purification. The aqueous filtrate is evaporated to a small volume on the water-bath and allowed to cool. A beautiful white crystalline product quickly deposits, weighing from 5.6 to 5.8 g., depending on the volume of the solution. When recrystallized from water this separates in the form of large, transparent, 4-sided plates and melts at 272–274°, the correct melting point of hydro-uracil.

Analysis. Calc. for C₄H₆O₂N₂: N, 24.56. Found (Kjeldahl): 24.69.

The calculated quantity of hydro-uracil is never obtained in these reductions; this is due to the fact that the gum arabic is partially decomposed during the evaporation of the hydrochloric acid solution giving a sirup which always retains a small amount of pyrimidine that cannot be recovered. That the reduction, however, is quantitative is shown by the application of Wheeler and Johnson's color test to the reduction solution. When 3 cc. of the solution, corresponding to 0.09 g. of pyrimidine, is added to an equal volume of acetone to remove the platinum, and the color test is then applied no purple condensation product is obtained, showing the absence of unreduced product. One mg. of uracil gives a decided bluish-pink or lavender color within a short time when subjected to a similar treatment.

The Colloid Support.—In order to study the effect of various amounts of gum arabic on the progress of the reduction of uracil to hydro-uracil a series of experiments was performed using in each case 3 g. of uracil,

Gum arabic, g	0.2	0.5	1.0	2.0	5.0
H ₂ absorbed, cm	21.2	24.5	23.3	22.4	17.3
(1 cm. equals 26 cc. of hydrogen un					

^{*}A special equipment was constructed for our work whereby several experiments can be run independently at the same time.

100 cc. of water, 10 cc. of 10% chloroplatinic acid and various amounts of gum arabic. The time of each run was 7 hours and 40 minutes.

In each of the above experiments the platinum remained in the colloidal state throughout the operations and the results show that the rate of absorption of hydrogen is not materially affected by the quantity of gum arabic used. Rideal⁵ states that there is an optimum amount of gum arabic for each catalyst, corresponding to about 4 mg. per 10 mg. of platinum, and that amounts in excess of this tend to retard the rate of absorption of hydrogen. He arrived at this conclusion from results obtained during the study of the reduction of the propiolic acid. Our results show that concentrations of gum arabic 25 times as great as those that retarded or stopped the reduction of propiolic acid exerted very little, if any, influence on the reduction of uracil to hydro-uracil, and that such an optimum does not exist in the case of this pyrimidine.

Several experiments were made in an effort to substitute pepsin and trypsin for gum arabic as colloid supports in the reduction of uracil to hydrouracil. For example, 3 g. of uracil, 0.5 gm. pepsin, 100 cc. of water and 5 cc. of chloroplatinic acid were used in one experiment. During 2 hours and 15 minutes an absorption of 1 cm. (26 cc.) had taken place. The platinum had separated and fallen to the bottom of the flask, so 3 cc. more chloroplatinic acid was added and during the next 2 hours and 40 minutes an absorption of 5.3 cm. (138 cc.) was obtained, making a total of 6.3 cm. Gum arabic was then added with more chloroplatinic acid and the reduction completed. The absorption was much slower than usual, showing that pepsin probably exerts an anticatalytic effect. When this experiment was duplicated, using gum arabic as colloid support, an absorption of 23 cm. was obtained in the same length of time, using only 5 cc. of chloroplatinic acid as catalyst.

In a similar experiment using trypsin as colloid support an absorption of 9.6 cm. was obtained during a run of $7^1/_2$ hours, with 5 cc. of chloroplatinic acid, at the end of which time the platinum had completely separated. Gum arabic and 2 cc. more of chloroplatinic acid were then added and the reduction carried to completion. The reduction proceeded normally after the addition of the gum arabic, showing that the trypsin had no anticatalytic effect, as was observed in the case of pepsin.

Effect of Temperature and Shaking on the Rate of Absorption of Hydrogen.—Three g. of uracil, 0.5 g. of gum arabic, 100 cc. of water and 5 cc. of 10% chloroplatinic acid were placed in the reduction flask and the reduction started as in previous experiments. During one hour and 40 minutes 75 cc. of hydrogen was absorbed, which corresponds practically to the quantity necessary for the reduction of the platinic acid to colloidal platinum. No further absorption took place at ordinary temperature.

⁵ Rideal, This Journal, 42, 749 (1920).

An increase in temperature caused an immediate increase in absorption of hydrogen, and at 75° the rate was normal and continuous until 600 cc. of hydrogen gas was taken up. In other words, the rate of reduction is increased by rise in temperature. Furthermore, it is not necessary to increase the proportions of the catalyst to produce this effect.

The rate of hydrogen absorption is also influenced greatly by the intensity of agitation or shaking. In an experiment in which the motion of the reduction flask was controlled by means of lights placed in the armature circuit of the motor so as to produce a moderate or a rapid vibration of the reduction flask, it was observed that the rate of absorption could be increased 100% by intense agitation. Within 45 minutes an absorption of 175 cc. of gas was obtained when a 60-watt lamp was introduced into the armature circuit, while 405 cc. of hydrogen was absorbed in the same period of time when this light was replaced with a 100-watt lamp. Using the same proportions of reagents as above, it was found that by rapidly shaking the mixture it was possible to bring about an absorption of the calculated volume of hydrogen (600 cc.) in 1.5 hours at 75° .

Effect of Chlorides of Sodium, Potassium, Calcium and Magnesium, and of Sulfur Compounds on the Reduction of Uracil.—In a series of experiments using 3 g. of uracil, 1 g. of gum arabic, 100 cc. of water, 10 cc. of 10% chloroplatinic acid and 1 g. each of sodium, potassium, calcium and magnesium chlorides it was observed that these chlorides exerted no influence on the progress of the reduction of uracil to hydro-uracil. The reduction in each case was complete and the calculated amount of hydrogen was absorbed in the same time required for the reduction of uracil in the absence of the above salts. From 2.6 to 2.9 g. of hydro-uracil was isolated from each experiment, showing that the presence of the salts adds no difficulties in the isolation of the hydro-uracil.

In an experiment in which a sample of uracil was used containing enough thio-uracil to be detected by the nitroprusside test, an absorption of hydrogen equal to the amount required for the reduction of the chloroplatinic acid was obtained, showing that sulfur even in such small amounts completely prevents the reduction. This same sample after purification to remove sulfur (negative nitroprusside test) and repeated recrystallizations from water could then be reduced, but it required twice the platinum concentration for reduction that it did after further purification by boiling with monochloro-acetic acid which insures the complete removal of the sulfur. In an attempt to reduce pure thio-uracil a colloidal solution of the platinum was not obtained during 7 hours' treatment, using the same conditions as described above. No reduction was obtained when the platinum was first reduced to the colloidal state and the thio-uracil then added, even with much larger concentrations of platinum.

Effect of the Addition of Catalyst in Portions on the Reduction of Uracil

Containing Traces of Sulfur.—The following experiments were made on a sample of uracil containing traces of thio-uracil; in each experiment 6 g. of uracil, 2 g. of gum arabic and 200 cc. of water were used and the chloroplatinic acid was added as described below; otherwise the conditions of the experiments were the same as in the preceding reductions. With 12 cc. of chloroplatinic acid an absorption of 300 cc. of hydrogen was obtained in 2 hours, at the end of which time the absorption had practically ceased, so 10 cc. more of chloroplatinic acid was added. During the next 5 hours 900 cc. of hydrogen was absorbed, bringing the total to 1200 cc., the calculated amount required for complete reduction of the pyrimidine. In another experiment, after the addition of 22 cc. of chloroplatinic acid at first the reduction proceeded for 5 hours before coming to a standstill and 650 cc. of hydrogen was absorbed. Five cc. more of chloroplatinic acid carried the reduction to the end in 4 hours in which time 550 cc. of hydrogen was absorbed. A total of 27 cc. of chloroplatinic acid was required for the complete reduction. In another experiment in which the chloroplatinic acid was added in portions of 5, 7, 5 and 3 cc. the final absorptions were 40, 380, 500 and 320 cc. of hydrogen, respectively. Only 20 cc. of chloroplatinic acid was required for complete reduction. When this was added in portions of 12, 5 and 3 cc., the corresponding absorptions were 240, 650 and 350 cc. during $1^3/4$, 4 and $2^1/2$ hours, respectively. From each of the above experiments hydro-uracil was isolated in amounts varying from 5.6 g. to 5.9 g., showing that the reduction proceeded to completion in each case. These experiments show that better reduction is obtained when the catalyst is added in portions to compounds containing small amounts of "poisons" than all at the same time.

The Influence of the Solvent on the Reduction of Uracil in the Presence of Colloidal Platinum and Palladium.—The solubility of uracil in the different solvents is, as a rule, so small that only a few solvents are suitable for the reduction work. This is especially true of the organic liquids in which uracil is practically insoluble. The best solvent for uracil is water, in which the solubility is not appreciably affected by the presence of acids, but is greatly increased by alkalies; hence a study of the reduction process in alkaline solution, if successful, would add greatly to the production of hydro-uracil in quantity.

A number of experiments were carried out in alkaline solution in an effort to reduce this pyrimidine, and in none was there any evidence of the absorption of hydrogen after the amount necessary for the reduction of the chloroplatinic acid or palladium chloride used as the catalyst, in runs varying from one to three days, using the conditions employed in the preceding experiments.

In experiments carried out with glacial acetic acid, as well as dilute acetic acid of different strengths as solvents, it was shown that this medium is

equally good but no better than water for the reduction of uracil. Various strengths of hydrochloric acid when added to the reduction solution produced no effect on the reduction. Of course, in each of the experiments except those carried out in alkaline solution some hydrochloric acid was present resulting from the reduction of the chloroplatinic acid.

Experiments carried out under identical conditions showed that the reduction proceeded more rapidly with colloidal platinum than with colloidal palladium when equal weights of the two materials were used; however, the differences were never large and both are applicable for the reduction of uracil to hydro-uracil.

Summary

- 1. Uracil is converted quantitatively into hydro-uracil (β -lactylurea) by treatment with hydrogen in the presence of colloidal platinum or palladium.
- 2. Since hydro-uracil has been shown to undergo hydrolysis smoothly to β -alanine⁶ our method of reduction, therefore, offers an easy and practical method of converting uracil directly into β -alanine. From a biochemical point of view this result is one of especial interest and importance.

New Haven, Connecticut

[Contribution from the Chemical Laboratory of the University of Washington]

BETA-PHENOXYPROPIONIC ACID AND SOME OF ITS DERIVATIVES. CHROMANONE

By S. G. POWELL RECEIVED AUGUST 6, 1923

In the course of an investigation of certain unsaturated phenyl ethers, which is to be reported later, a considerable quantity of β -phenoxypropionic acid was required. The only method then available for the preparation of this compound was that of Bischoff¹ which depends upon the action of sodium phenoxide on sodium β -iodopropionate. Unfortunately, the latter is difficult to obtain; moreover, the yield of β -phenoxypropionic acid under the most favorable conditions is only 20%. This paper describes a convenient method for obtaining this acid from the corresponding alcohol.

In preparing some derivatives of the acid, an attempt to purify a sample of β -phenoxypropionyl chloride by distillation resulted in the isolation of the hitherto unknown chromanone. This compound and some of its derivatives are also described.

⁶ Weidel and Roithner, Monatsh., 17, 183 (1986). Lengfeld and Stieglitz, Am. Chem. J., 15, 221, 517 (1893).

¹ Bischoff, Ber., 33, 928 (1900).

Attempts to oxidize γ -phenoxypropyl alcohol with alkaline permanganate by the method of Fournier² were not successful. Oxidation with neutral permanganate, however, gave results which were highly satisfactory, although by no means quantitative. It should be mentioned here that this method is being further investigated, not only as applied to this acid, but also to other β -aryloxy fatty acids. The yield by the method described in this paper varies between 32 and 45% when 10 g. or less of the alcohol is oxidized at one time, but falls off materially when larger quantities are used. Thus 10 g. of the alcohol gave 5 g. of the acid, whereas 40 g. gave only 7 g. As the success of the oxidation depends upon keeping the temperature low, the poorer yield in the larger runs may be due to imperfect cooling of the larger volume of solution. In the smaller runs the yield was not improved by using an excess of permanganate, although about half of the alcohol was recovered unchanged.

+ HCl. This compound is more readily obtained, however, by the dehydration of the free acid by means of phosphorus pentoxide. It resembles very closely the 6-methyl-chromanone described by V. Auwers and Krollpfeiffer.³ Thus, it reacts normally as a ketone with hydroxylamine forming an oxime, and condenses with benzaldehyde to benzal-chromanone.

The preparation of other chromanones and their derivatives by this same general method will be described in a later paper.

Experimental Part

 γ -Phenoxypropyl Alcohol, C₆H₅OCH₂CH₂CH₂OH.—The γ -phenoxypropyl alcohol used in this work was prepared by a modification of the method described by Rindfusz⁴ who obtained it in 75% yield by treating an absolute alcoholic solution of sodium phenoxide with trimethylene chlorohydrin. By using an aqueous solution of sodium phenoxide, in which the chlorohydrin is completely soluble, the use of metallic sodium and absolute alcohol is avoided, the reaction is completed in a much shorter time, and slightly better yields are obtained.

To a solution of 250 g. of phenol in 1000 g. of 10% aqueous sodium hydroxide is added 188 g. of trimethylene chlorohydrin, and the clear solution is heated to boiling under a reflux condenser. About 3 minutes after the solution begins to boil it separates into two layers and the reaction is practically complete at this point. To insure com-

² Fournier, Bull. soc. chim., [4] 5, 920 (1909).

³ Auwers and Krollpfeiffer, Ber., 47, 2585 (1914).

⁴ Rindfusz, This Journal, 41, 668 (1919).

plete reaction, however, the boiling is continued for 30 minutes. The mixture is cooled, the phenoxypropyl alcohol taken up in ether, the ether solution washed with dil. sodium hydroxide solution, then with water, and finally dried over sodium sulfate. After removing the ether, the oily residue is heated when the phenoxypropyl alcohol distils at 160° (25 mm.); yield, 240 g., or 80%.

β-Phenoxypropionic Acid, $C_6H_5OCH_2CH_2COOH$.—This compound has been prepared by Bischoff¹ who obtained it by treating sodium β-iodopropionate with sodium phenoxide. It is more conveniently prepared by the oxidation of the corresponding alcohol by the following method.

Ten g. of γ -phenoxypropyl alcohol is added to a solution of 30 g. of crystallized magnesium sulfate in 100 cc. of water contained in a narrow bottle immersed in a pan of cold water. The mixture is kept well stirred with a mechanical stirrer, and 280 cc. of 5% potassium permanganate solution is added drop by drop over a period of several hours, while the temperature is maintained at about 15–20°. The stirring is continued until the color of the permanganate disappears. A slight excess of sodium bisulfite is then added and the mixture is acidified with 50% sulfuric acid, when the β -phenoxypropionic acid separates as an oil which partially solidifies as it cools. The oily mass is dissolved in ether and the ether solution extracted with 5% sodium hydroxide solution. The alkaline extract is acidified with dil. sulfuric acid when the phenoxypropionic acid separates in shiny, needle-like crystals. After the mixture has cooled, the acid is filtered off and recrystallized from hot water from which it separates in long needles melting at 98°. The yield varies between 3.5 g. (32%) and 5 g. (45%). The ether solution from which the acid has been extracted contains unoxidized alcohol, which is recovered and treated again.

Ethyl β-Phenoxypropionate, C₆H₅OCH₂CH₂COOC₂H₅.—Forty g. of the acid is dissolved in 400 cc. of absolute alcohol previously saturated with dry hydrogen chloride and the solution boiled under a reflux condenser for one hour. Most of the alcohol is then distilled, the residue diluted with water, and the ester taken up in ether. The ether solution is washed with dil. sodium carbonate solution, then with water, and finally dried over sodium sulfate. After removal of the ether, the residue is heated, when the ester distils to the last drop at 170° (40 mm.). The product is a colorless oil with a characteristic, very persistent odor; yield, 42 g., or 90%.

Analysis. Subs., 0.2009: CO₂, 0.5020; H_2O , 0.1432. Calc. for $C_{11}H_{14}O_3$: C, 68.1; H, 7.2. Found: C, 68.1; H, 7.9.

β-Phenoxypropionyl Chloride, $C_6H_0OCH_2CH_2COC1$.—A solution of 20 g. of β-phenoxypropionic acid in 60 g. of thionyl chloride is heated to 100° for 30 minutes, and then distilled. Two main fractions are obtained, one boiling at 159–160° (50 mm.) and the other boiling at 237° (50 mm.). The lower-boiling fraction is chromanone, while the higher-boiling has not been further investigated except to determine that it is halogen-free. When, however, the acid is gently warmed for a few seconds with only a slight excess of thionyl chloride, a liquid of irritating odor is produced which yields the corresponding amide with ammonia.

 β -Phenoxypropionamide, $C_6H_5OCH_2CH_2CONH_2$.—The crude reaction mixture from 3 g. of the acid and 3 g. of thionyl chloride is added drop by drop to an excess of concd. aqueous ammonia. After standing overnight, the precipitated amide is filtered off and recrystallized from hot water, from which it separates in shiny needles melting at 119°.

Analysis. Subs., 0.5110: 30.6 cc. of 0.1 N H_2SO_4 . Calc. for $C_9H_{11}O_2N$: N, 8.48. Found: 8.38.

Chromanone.—To a solution of 25 g. of β -phenoxypropionic acid in 200 cc. of dry benzene, 50 g. of phosphorus pentoxide is added, and the mixture is refluxed for one hour. The benzene solution is decanted and the dark colored mass of phosphorus compounds extracted several times with boiling benzene. The united benzene solutions are washed with a little dil. sodium hydroxide solution, then with water and finally dried with a little calcium chloride. The benzene is removed by distillation from the waterbath and the residue distilled. The chromanone forms a colorless, highly-refracting liquid, with a very pleasant lemon-like odor. It boils at 160° (50 mm.) and on standing solidifies to a mass of hard crystals melting at 38.5° .

Analysis. Subs., 0.2554: CO₂, 0.6810; H₂O, 0.1287. Calc. for $C_0H_8O_2$: C, 73.0; H, 5.4. Found: C, 72.7; H, 5.6.

Chromanone Oxime.—Three g. of chromanone and 3 g. of hydroxylamine hydrochloride are dissolved in 50 cc. of alcohol, 6 g. of potassium carbonate is added and the whole boiled under a reflux condenser on the water-bath for 6 hours. The product is poured into water when the oxime separates and is filtered off. It is purified by dissolving it in hot benzene and precipitating with petroleum ether. It forms glistening, needle-like crystals melting at 140°.

Analysis. Subs., 0.2416: (Kjeldahl) 14.5 cc. of 0.1 N H₂SO₄. Calc. for C₉H₈O₂N: N. 8.6. Found: 8.4.

Benzal-chromanone.—Three g. of chromanone and 4 g. of benzaldehyde are dissolved in 50 cc. of alcohol, the solution is heated almost to boiling, and 10 cc. of coned. hydrochloric acid added drop by drop. After standing for several days the benzal-chromanone which has separated is filtered off and recrystallized from alcohol, from which it separates in long yellow needles melting at 112°.

Analysis. Subs., 0.2130: CO_2 , 0.6314; H_2O , 0.1034. Calc. for $C_{18}H_{12}O_2$: C, 81.4; H, 5.1. Found: C, 80.9; H, 5.4.

Summary

- 1. The method of preparation of γ -phenoxypropyl alcohol has been simplified.
- 2. β -Phenoxypropionic acid has been prepared by oxidation of the corresponding alcohol.
 - 3. Some derivatives of β -phenoxypropionic acid have been prepared.
 - 4. Chromanone and some of its derivatives have been prepared.

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[Contribution from the Department of Chemistry, Columbia University, No. 423]

EXPERIMENTS WITH TWO METHODS FOR THE STUDY OF VITAMIN B

By H. C. Sherman and Harriet Edgeworth Received August 6, 1923

The further progress of our knowledge of the vitamine must depend largely upon the development of methods for the experimental study of these substances which shall be both practicable and quantitative. When such methods are sufficiently developed they can be applied to the quantitative measurement of the concentration of the vitamin at successive steps in attempts to isolate the substance from natural sources and bring it to a condition of maximum purity for the determination of its chemical nature. Moreover, the importance of vitamin B as a factor in food values makes it urgently desirable that quantitative methods of known precision be applied in all studies of the vitamin contents of different foods or of the same food before and after heating or other treatment to which foods may be subjected.

As has been fully explained elsewhere^{1,2} such methods imply feeding to a suitable organism, in or with an otherwise adequate diet, known amounts or proportions of the material to be tested as the sole source of the vitamin in question.

In this and the two following papers dealing with vitamin B, we use this term to designate the growth-promoting, water-soluble B vitamin without regard to the question as to whether this is or is not identical with the antineuritic substance. Hence, we have taken the growth of young rats rather than the prevention or cure of polyneuritis in pigeons as our principal criterion. Several investigators have worked actively in the belief³ that experiments based on acceleration of yeast growth could serve the same purpose as those based on rat growth and in a quicker, more economical and more readily controllable way. Different methods of ascertaining the stimulating or growth-promoting effect of the vitamin upon the yeast were proposed: (a) counting the cells produced; (b) measuring the carbon dioxide produced; (c) measuring the increase in volume of yeast cells; (d) weighing to determine the increase in yeast gravimetrically.

The counting of yeast cells, even as reported by those who have appeared to have most confidence in this method, has yielded data showing such wide variations in duplicate tests as to preclude its employment in quantitative investigations.

- ¹ Chick and Hume, J. Biol. Chem., 39, 203 (1919).
- ² Sherman, LaMer and Campbell, This Journal, 44, 165 (1922).
- ³ For further discussion, see Sherman and Smith, "The Vitamins," Chemical Catalogue Company, New York, 1922, pp. 72-75.

In the estimation of yeast growth (or activity) by measurement of the carbon dioxide produced, there is the difficulty that the difference in carbon dioxide pressure at the two surfaces of the liquid in the fermentation tube permits a loss of carbon dioxide by passage through the solution. Obviously also even small changes in temperature may result in further error. This method therefore does not seem promising from a quantitative point of view.

In measuring the volume of the yeast, the fact that yeast-substance is largely protein, having an iso-electric point on either side of which it will show differences in amount of swelling, depending on the hydrogen-ion concentration of the medium, must be taken into account and plainly detracts much from the ease and precision which might otherwise be expected of this method.

The gravimetric method seemed, therefore, the most promising from the standpoint of quantitative accuracy of results.

Yeast was made up for seeding from a Fleischmann yeast cake according to the method of Williams, 4 and was grown for 18 hours at 30° in a constant-temperature oven, in one of the two media described below.

As source of vitamin B we selected dried skimmed milk, as a material readily available and easily kept uniform throughout the investigation, easy and accurate of manipulation, and usable either in the dry state or reconstituted as fluid skimmed milk by mixing with nine times its weight of water. It was desired to employ a typical and natural form of vitamin B free from any danger of having been altered or fractioned by chemical or physical treatment. It was also thought best, in view of the experience of this and other laboratories and of Osborne's suggestion that vitamin B may occur naturally in chemical combination with the proteins of some foods, to avoid the use of any method which should involve the necessity of employing extracts of the food to be tested.

Experiments with the Growth of Yeast

Using the Medium of Williams.—This medium contains asparagine, 1.5 g.; calcium chloride, 0.25 g.; magnesium sulfate, 0.25 g.; monopotassium orthophosphate, 2.0 g.; ammonium sulfate, 3.0 g.; and sugar 20.0 g. per 100 cc. It was made up in lots of one liter divided into aliquot portions of 100 cc. each, placed in Erlenmeyer flasks stoppered with cotton and sterilized in an autoclave at 10 pounds' pressure for 15 minutes. To each portion, when cooled to 30°, was added 1 cc. of yeast suspension containing 0.3 mg. of yeast prepared according to the method of Williams. These portions were then incubated at 30° for 18 hours, at the end of which time 1 cc. of U.S.P. formaldehyde was added to each flask to prevent further growth of the yeast, and the contents were subsequently filtered through

4 Williams, J. Biol. Chem., 42, 259 (1920).

a weighed Gooch crucible prepared according to Williams, washed, and dried at 102° to constant weight. Parallel tests were made with the addition of various amounts of the skimmed milk used as source of vitamin B, sometimes as purchased, sometimes after heating for 6, 12, 24, or 48 hours at 100°. The control involved two tests (1) of medium and yeast without added source of vitamin, (2) of medium plus the amount of milk used as source of vitamin in each experiment.

As this medium itself contained no insoluble material, the sum of the weights obtained in the two control tests just mentioned was taken as the correction to be subtracted from the gross weighing obtained in each test, the remainder showing the amount of yeast growth due to the material added as source of vitamin.

The concentrations of hydrogen ion in (a) the control with yeast only, (b) the medium plus yeast plus 0.4 g. of unheated skim milk powder, (c) the medium plus yeast plus 0.4 g. of skim milk powder heated for 48 hours at 100°, were determined before and after incubation and found to be (a) before incubation, PH 4.4; after incubation, PH 5.5; (b) before, PH 5.7; after, PH 7.1; (c) before, PH 5.5; after, PH 7.0.

While the media seem to become slightly less acid during the process of incubation, the change is not such as to interfere with the correction of results for precipitated milk protein as described above.

In a series of determinations in which 0.4 g. of the milk powder was tested, the average results were as follows.

	G.
Wt. of insoluble matter from medium + yeast	0.0030
Wt. of insoluble matter from medium + milk	1088
Total wt. to be subtracted	
Average gross wt. in tests	
Accelerated growth due to the milk	0454

The average results of about 200 quantitative tests made by this method with or without the introduction of various amounts of the milk powder as source of vitamin B are shown in Table I.

It will be seen that the results are such as amply to justify quantitative discussion. The averages of the total, and of the accelerated growths observed show probable errors which in all cases are less than 2%, and in most cases are less than 1% of the quantities concerned. The accelerated growth of the yeast shows progressive increase with the quantity of milk powder added up to 0.4 g. This amount was therefore used in testing for the effect of heat upon the vitamin B content of the milk powder as indicated by this method. The effects attributable to heating at 100° for from 12 to 48 hours are in our judgment too small to permit of definite conclusions as to whether a measurable amount of vitamin B was thus destroyed.

Thus our experiments show that the growth of yeast in the Williams medium is a process capable of acceleration by the addition of vitamin-containing material and that this acceleration of yeast growth can be determined gravimetrically with a satisfactory degree of precision. As yet, however, there is not sufficient evidence that the Williams medium

Table I Summary of Results by the Gravimetric Yeast Method Using Williams' Medium

Milk powd added	Heating at 100°			rowth Probable		ted growth Probable
G.	Hours	tests	G.	errora	G.	errorb
Non	e	60	0.0031	± 0.00004	• • • •	
0.1	unheated	17	.0174	\pm .00027	0.014	± 0.0003
.2	unheated	14	.0285	\pm .00026	.026	± .0003
.4	unheated	39	.0482	\pm .00025	.045	\pm .0003
.6	unheated	16	.0430	\pm .00027	.040	± .0003
.4	12	19	.0390	$\pm .00040$.036	$\pm .0004$
.4	24	13	.0390	\pm .00036	.036	$\pm .0004$
.4	48	20	.0377	$\pm .00056$.035	\pm .0006

^a Computed according to the classical method as described, for example, by Jevons, "Principles of Science," The MacMillan Co., London and New York, 1905, p. 387.

contains such favorable proportions of all other essential nutrients as to justify the assumption that acceleration of growth upon addition of food material to this medium is necessarily attributable solely to the introduction of vitamin B, and the experiments of Fulmer and his co-workers^{5,6} published while our own work was in progress tend strongly to the opposite view. Experiments with the medium of Fulmer, Nelson and Sherwood were therefore undertaken.

Using the Medium of Fulmer, Nelson and Sherwood.—For the reason above given, the method of counting cells did not seem suitable for our work and we have, therefore, tried to adapt the gravimetric method to the use of this medium, which contains undissolved calcium carbonate and precipitated phosphate. These insoluble buffers apparently yield variable amounts of residue at the end of the incubation period, for neither by drying and weighing nor by ignition of the dry residue and subtraction of the mineral matter, were we able to obtain satisfactory gravimetric measurements of yeast growth when this medium was used.

Experiments with Growth of Rats

The rat was preferred as experimental animal because it has been best standardized by previous work. Several rats of the same litter and approximately the same size were, when 28 to 30 days old, divided into groups as closely matched as possible in size and in distribution of the

^b Computed by the usual rule that the probable error of the difference of two means is the square root of the sum of the squares of their probable errors.

Fulmer, Nelson and Sherwood, This Journal, 43, 191 (1921).

⁸ Nelson, Fulmer and Cessna, J. Biol. Chem., 46, 77 (1921).

sexes, some groups receiving the skimmed milk powder unheated and others receiving heated milk powder as stated beyond. This skimmed milk powder was analyzed with the following results: moisture, 3.0; fat, 0.3; protein, 33.3; ash, 7.2; and carbohydrate by difference, 56.2%. It was fed mixed with the other food materials in a diet composed of starch, 50; skimmed milk powder, 40; purified butter fat, 9; and sodium chloride, 1%. Except for a different distribution of calories as between starch and fat, this diet corresponds fairly closely to the whole-milk-starch-fat diet which Osborne and Mendel have shown to be adequate.

Furthermore, unpublished experiments in this Laboratory have shown that 40% of the food mixture is about the minimum proportion of skimmed milk powder for optimum growth when this constitutes the sole source of protein and water-soluble vitamin and that when growth is retarded by further dilution of milk powder with starch, vitamin B becomes the first limiting factor in the growth of young rats. Hence, the use of 40% of skimmed milk powder in the food mixture for the experiments on growth of rats was considered analogous to the addition of 0.4 g. of this powder per 100 cc. of Williams' medium in the experiments upon the growth of yeast.

The experiments with rats were carried out in three series, (1) in the autumn of 1920, (2) in the summer of 1921, (3) in the autumn of 1921. In all cases the animals were weighed weekly and the feeding experiments continued for eight weeks. Using the diet described above, the gains in weight during the eight weeks, averaged for all the rats in each of the three series separately, with the probable errors of these averages, were as shown in Table II.

Table II

Gains in Weight of Rats during Eight Weeks on Experimental Diet Containing
Unheated Milk Powder

	No. of rats	Av. gain G.	Probable error
First series	11	125	± 4.0
Second series	39	92	± 2.2
Third series	14	99	± 2.9

Here it will be seen that averages of 11 to 39 animals in a series are subject to probable errors of about 2 to 3% of their numerical values. The differences in average gains from season to season are sufficient to emphasize the importance of making quantitative comparisons directly with control groups fed simultaneously rather than with pre-established normal rates of growth alone. The latter, however, are valuable as a check upon all work of this character.

The differences in general average gains between all animals receiving milk powder unheated, and all those receiving the same after heating are shown in Table III.

Table III

Gains in Weight of Rats during Eight Weeks on Diets with Unheated as

Compared with Heated Milk Powder

Time of heating milk powder at 100° Hours	No. of rats	G. A	v. gain Probable error	those	erence from on unheated ood Probable error	Food eaten G.
Unheated	64	100	± 2.0			537
6	28	86	± 2.7	14	± 3.4	513
12	23	77	± 1.8	23	± 2.7	501
24	21	59	± 2.5	41	± 3.4	439
48	22	40	± 3.3	60	± 3.9	406

Here it is plain that the differences in growth are too large to be accidental; but it is not plain whether the slower growth on the heated food is due to heat destruction of vitamin or to other causes. The last column of Table III shows that with increasing heat treatment of the food there was a progressive decrease in the amount of food consumed. The decreased food consumption would probably be sufficient to account for the decreased gain in weight whether heat destruction of vitamin had occurred or not. Since vitamin B promotes appetite it might be argued that decreased food intake is due to decreased vitamin content of the food through its heating; but the heating might make the food less appetizing in other ways, as through changing its flavor, and there is some reason to believe that this was actually a factor in these experiments because at the time they were made we had not entirely eliminated uneven heating, with consequent occasional local over-heating of the food. The thorough mixing, of the food would result in distributing through the whole food mixture any particles which might have acquired a cooked flavor through local over-heating. In subsequent experiments described in the paper which follows, the heat treatment was more perfectly controlled, the food consumption was more uniform and the differences in gains of weight attributable to dry heating of the food at 100° practically disappear.

When 10 animals on each variation of the heat treatment were compared with 10 litter-controls receiving unheated food, the average results were as shown in Table IV.

Table IV Comparisons of Gains and Probable Errors on Averages of Groups of Ten

Time of heating milk powder at 100° Hours	Av. gain G. Probable error	Decreased gain on heated food G. Probable error
Unheated	99 ± 3.6	
. 6	97 ±3.6	2 ± 5.1
Unheated	97 ±3.6	
12	86 ±2.4	11 ±4.3
Unheated	100 ±2.2	
24	56 ±3.6	44 ±4.2
Unheated	116 ±2.2	
48	51 ±4.9	65 ± 5.4

As explained above, these experiments do not answer the question as to whether the heat treatment here employed destroyed a measurable proportion of the vitamin. They do eliminate seasonal influences and illustrate well the degree of precision to be expected from this method when dealing with averages of groups of ten. The average gains in groups of 10 rats on unheated food are subject to probable errors of 2 to 4% while in those groups in which heating of food has decreased the average rate of gain the results are more variable and the probable errors are relatively larger.

Summary and Conclusions

The purpose of this work was to examine the availability of the gravimetric yeast-growth method and of the rat-growth method for quantitative study of vitamin B.

The gravimetric yeast-growth method using the Williams medium and procedure yielded consistent results. The coefficients of variation and the probable errors of the averages obtained in the different series were within limits quite satisfactory for work in this field, the probable errors being of the order of 1% of the observed numerical values. This method is, however, open to the objection that the increased growth of yeast which it measures may be due to the introduction of other substances favorable to yeast growth and is therefore not necessarily a measure of relative amounts of vitamin B. The medium devised by Fulmer, Nelson and Sherwood to overcome this objection did not, in our hands, prove adaptable to use with the gravimetric method of determining the growth of the yeast.

The rat-growth method also yielded quantitative results. It was found desirable to use rats four weeks of age for these experiments and to continue them upon the experimental diets for eight weeks. So far as is practicable each experimental animal should have a closely comparable control, taken at the same time from the same litter and of approximately the same initial size so that a series of comparisons can be made between animals confidently regarded as directly and accurately comparable. The conclusions reached through such comparisons should then be verified by comparison of the general averages of groups so large as to insure that individual peculiarities cannot appreciably affect the final result. In the work here recorded averages were drawn in each of these ways, and the probable errors of these averages were found to be of the order of 2 to 4% of their numerical values.

While the rat-growth method involves somewhat larger probable errors than the gravimetric yeast-growth method as here used, the results can be interpreted in terms of vitamin B with much greater certainty and we therefore consider the use of the growing rat to be the preferable method.

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[Contribution from the Department of Chemistry, Columbia University, No. 424]

A CRITICAL INVESTIGATION AND AN APPLICATION OF THE RAT-GROWTH METHOD FOR THE STUDY OF VITAMIN B

By H. C. Sherman and Adelaide Spohn

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For the present investigation white rats were selected as the experimental animal and dried skimmed milk as the vitamin-containing food. Our own experience and what we have been able to learn of the experience of others, lead to the belief that more regular results, and therefore a higher degree of precision in quantitative studies, may be expected from experiments with rats than with pigeons. While the gravimetric form of the Williams yeast-growth method is also capable of yielding satisfactorily quantitative data, the use of rats permits the interpretation of results in terms of vitamin B with much greater certainty and is therefore the preferable method.¹

Selection and Care of Experimental Animals.—The white rats used were placed upon the experimental diets when 28 or 29 days old, this being the standard age adopted in our Laboratory for the separation of young rats from their mothers. These young (four weeks old) rats weighed in all cases between 30 and 65 g., in most cases between 40 and 50 g. The animals all came from mothers on similar diets (a mixture of dried whole milk and ground whole wheat, with or without the addition of meat), with the further precaution that, in each experiment, equal numbers of comparison and control rats came from mothers on exactly the same diet.

The young rats were assigned to the diets to be compared in the following manner. If, for example, in one experiment there were five variations of diet to be compared and ten rats were to be fed on each variation, it would very likely be necessary to make use of six to eight litters to obtain the 50 rats required. Each litter was distributed over the five variations of diet as far as it would go so that each rat on each diet had litter-controls on other diets, and the entire 50 rats were so distributed in the assignment that the total weight of the ten rats and the number of males and females on each modification was practically the same. (At this age the difference in size between the sexes is much smaller than the individual variation in either sex.)

The experiments were continued for eight weeks, from the beginning of the fifth to the end of the twelfth week of the rat's life, this being the period during which the rat grows most rapidly if normally fed. It was demonstrated by continuing several of the experiments for a period of 50%

¹ Sherman and Edgeworth, This Journal, 45, 2712 (1923).

longer time that this extension of the experimental period beyond that here described did not yield any additional significant information.

In the (relatively few) experiments in which the milk was fed mixed with the rest of the diet, the animals were caged in lots of six to eight, each lot in a cage having a floor area of 28 by 35 cm. In all other experiments each rat was kept separately in a round galvanized iron wire cage 22.5 cm. in diameter and 20 cm. high with a raised screen floor which prevented access to the feces. No bedding was used nor was wood in any form accessible to the rats at any time. Fresh water and the basal ration were given freely. The cages were cleaned frequently, usually the group cages every day and the individual cages three times a week. The animals were weighed weekly (or oftener) and the amount of food consumed was determined and recorded for the same weekly intervals.

The Basal Diets.—The basal diets used were designed to be devoid of vitamin B and to contain all the other essential food factors in as nearly as possible the optimum proportions. No attempt was here made to supply vitamin C to the rats as they do not seem to need it and we do not know any source of vitamin C which could be depended upon to be entirely free from vitamin B. The two basal diets used in this work had the following composition.

Table I
Percentage Composition of Basal Diets

	Diet 94	Diet 107
Casein (purified by 60% alcohol) ^a	18	18
Salt mixture (Osborne and Mendel ²)	4	4
Butter fat	10	8
Cod liver oil	0	2
Starch	68	68
	100	100

^a The casein used in the basal rations was freed from vitamin B as follows. One liter of 60% (by weight) alcohol was poured upon 200 g. of casein and the mixture stirred for $^{1}/_{2}$ hour and then allowed to stand for $5^{1}/_{2}$ hours, filtered on a Büchner funnel and washed with 500 cc. of 60% alcohol; then again stirred with one liter of 60% alcohol as before, and this time the mixture was allowed to stand for 18 hours, then filtered and washed as before with 500 cc. of 60% alcohol and finally with 500 cc. of 90% alcohol to facilitate subsequent air-drying.

Tests of the Basal Diets.—In order to make sure that the basal diet contained the optimum amounts of its various constituents, it was fed in comparison with variations in which each ingredient in turn was increased in percentage, the increase replacing an equal weight of starch. Thus Diet 94 was compared with Diet 102 in which butter fat was increased to 15%; Diet 103, casein increased to 23%; Diet 105, salt

² Osborne and Mendel, J. Biol. Chem., 37, 572 (1919).

mixture increased to 5%; and Diet 104, casein replaced by meat protein. The results on these various diets were practically identical.

As a further test, similar variations in the constituents of the basal diet were introduced in experiments in which fixed amounts of milk were fed as sources of vitamin B. Again, no better results were obtained when the butter fat, or the casein, or the salt mixture was increased. Furthermore, it was shown by another series of experiments that the introduction of skimmed milk powder from which vitamin B had been extracted into the basal diet did not change the results. Each of the various modifications of both basal diets was tested on about 10 separate animals. Except for the condensed summary of a part of the data in Table III, the results of this extended and critical study of the basal diets are here omitted for the sake of economy of space. We believe it is amply established that the two basal diets used (Diets 94 and 107) furnish practically optimum amounts and proportions of all nutrients required by the rat except vitamin B, and that all increases in growth resulting from the addition of the milk to either of these diets may confidently be attributed to the vitamin B thus furnished.

The individual records of 10 rats receiving Diet 107 plus 8 cc. of milk per day are shown in Table II.

Table II
Weights of Ten Rats Receiving Diet 107 and 8 Cc. of Milk

				Age						l'otal
Rat	4	5	8	/eigh	8 ting	9 rams	10	11		ain in weeks
5960 (F)	49	63	79	86	87	80	78	81	91	42
5962 (F)	. 31	47	63	73	78	77	74	79	83	52
5965 (M)	. 55	71	81	80	82	84	85	89	96	41
5968 (M)	. 52	67	76	80	77	73	76	82	. 87	35
5994 (M)	. 58	73	87	93	91	84	84	87	93	35
5998 (F)	. 50	56	68	79.	80	83	86	85	87	37
6002 (M)			82	89	94	96	93	92	89	33
6040 (M)	. 56	70	77	82	78	72	77	79	85	29
6049 (M)			88	92	91	97	98	103	104	48
6055 (M)	. 44	63	77	85	85	80	83	84	92	48
Av.	51	65	. 78	84	84	83	83	86	91	40

A series of comparative tests in which the same amount of milk was fed with different modifications of the basal diet yielded the average results shown in Table III.

Diet 108 differed from Diet 107 in containing 13% of butter fat; Diet 109 in containing 23% of casein; Diet 110 in containing 5% of the Osborne and Mendel salt mixture. It will be seen that the variability of the animals on the different diets was of the same order and that the gains on the different modifications of the basal diet were essentially the same, the differences being even smaller than their probable errors.

Table III Comparison of Basal Diets 107, 108, 109, 110 (Fed with 8 Cc. of Milk)

Diet	No. of rats	Average gain G.	Probable error	Difference from diet 107 G.	Probable errorb	Average food in- take G.	Coefficient of variation of gains	
107	10	35	± 3.1	•		281	42	
108	12	32	± 3.6	- 3	±4.8	260	35	
109	11	35	± 2.4	0	± 3.9	275	34	
110	11	31	± 2.4	4	±3.9	268	38	

^a Computed according to the classical method as described, for example, by Jevons, "Principles of Science," The Macmillan Co., London and New York, 1905, p. 387.

The Question of the Best Amount of Milk to Feed in the Study of Heat Destruction of Vitamin B.—Two long series of experiments with the two

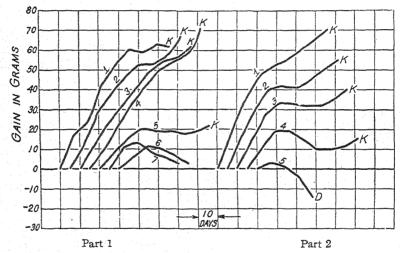


Fig. 1.—Part 1. Average-gain curves of rats on Diet 94 plus various amounts of skimmed milk.

Curve 1, + 15 cc. of milk; Curve 2, + 12 cc. of milk; Curve 3, + 10 cc. of milk; Curve 4, + 8 cc. of milk; Curve 5, + 6 cc. of milk; Curve 6, + 4 cc. of milk; Curve 7, + 2 cc. of milk.

Curve 1, + 12 cc. of milk; Curve 2, + 10 cc. of milk; Curve 3, + 8 cc. of milk; Curve 4, + 6 cc. of milk; Curve 5, no milk.

$$K = killed$$
 $D = died$

The last point on the curve is the average age and weight at death.

Curves 6 and 7 in Part I could not be completed, as some of the rats died before the end of the experimental period of eight weeks.

basal diets shown in Table I (above) were carried out for the purpose of finding the most advantageous amount of milk to feed in order to detect most readily any decrease in the vitamin B content which may result from

^b Computed according to the usual rule that the probable error of the difference of two means is the square root of the sum of the squares of their probable errors.

destruction by heat or from any other cause. The final average results of these two series of experiments are shown graphically in Parts 1 and 2, respectively, of Fig. 1. It will be seen from these curves that in the first series 8 cc. of milk per rat per day appeared to furnish an optimum amount of vitamin B, no further increase of growth resulting from larger feedings of milk. In the second series the rate of growth continued to increase with the amount of milk fed up to 12 cc. per rat per day, the largest amount here tested. The reason for this difference is not apparent; but in both cases it was found that the largest difference in weight gained from the same difference in milk fed is that between 6 cc. and 8 cc. per rat per day. Hence, for the purpose of the present investigation 8 cc. per rat per day was chosen as the best level at which to feed in order to detect any diminution in vitamin B content of the milk, since it is at this level that we found the largest difference in the total gain in weight for 8 weeks as compared with the next lower amount fed. (This presumably furnishes somewhat less than the optimum amount of vitamin B, since further addition of milk gave increased growth in many cases and in the general average; and it furnishes considerably more than the amount required for maintenance of constant weight which is the level of feeding found advantageous in some of our other experiments, as described in a subsequent paper.)

In another series of experiments the amount of milk given was varied in accordance with the weight of the rat, each animal receiving daily 5, 7.5, 10 or 12.5 mg. of the skimmed milk powder per gram of body weight. It was expected that this method might yield more regular results, but such did not prove to be the case. A comparison of the weight curves of the rats fed the same allowance of milk daily throughout the experiment, with those of rats whose daily allowance of milk was increased weekly in proportion to their increasing body weight, shows that the former are as uniform as the latter. Hence, in experiments in which the milk was fed separately from the basal ration we continued the method of giving each rat his predetermined daily dose regardless of changes in his body weight.

Since our plan contemplated experiments upon the heating of the milk in both the dry and the fluid condition, it seemed best for the sake of uniformity of conditions as affecting the experimental animals, to restore the dry milk to fluid form in all cases before feeding. This was done by mixing the weighed milk powder with distilled water in such proportions as to make 10 cc. of ("reconstructed") fluid milk from each gram of the skimmed milk powder. The daily dose of the fluid milk thus prepared was measured by means of a graduated pipet into a small feeding cup and placed in the cage at a uniform hour each day. Usually the rat consumed the daily allowance of milk promptly upon receiving it. When necessary in order to induce this, the water cup was removed until the milk had been consumed. This was necessary in only a few cases and then only for a

few feedings. In general there was no difficulty in securing prompt and complete consumption of the daily allowance of milk.

In several series of experiments the dry milk was fed mixed with the rest of the diet, replacing a smaller or larger part of the starch of Diet 94. The results are summarized graphically in Fig. 2, Part 1. The greatest

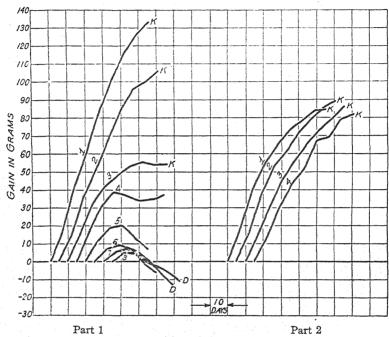


Fig. 2.—Part 1. Curve 1, Average-gain curve of rats on Diet 101 (30% milk); Curve 2, 100 (25% milk); Curve 3, 99 (20% milk); Curve 4, 95 (15% milk); Curve 5, 96 (10% milk); Curve 6, 97 (5% milk); Curve 7, 98 (2.5% milk); Curve 8, 94 (no milk).

Fig. 2.—Part 2. Curve 1, Average-gain curve of rats on Diet 100 (milk unheated); Curve 2, 100 (milk heated 6 hrs. at 100°); Curve 3, 100 (milk heated 24 hrs. at 100°); Curve 4, 100 (milk heated 48 hrs. at 100°). Heating was in dry air in these cases.

K = killed D = died

The last point on the curve is the average age and weight at death.

Curves 4, 5 and 6 in Part I could not be completed, as some of the rats died before the end of the experimental period of eight weeks.

difference in rate of growth for a given increment of milk in the diet was found between the diet containing 20% and that containing 25% of the skimmed milk powder in the dry food mixture. Hence on the same principle that 8 cc. was selected as the daily feeding in the experiments described above, we here selected 25% as the proportion of milk powder to be included in the food mixture in the cases in which the effect of heating was to be tested by feeding the milk in admixture with the rest of the food. Table

IV shows the average numerical results obtained from 11 comparisons of the three diets, 99, 100 and 101, which contained 20, 25 and 30%, respectively, of the dry skimmed milk in place of equal weights of the starch contained in Diet 94.

Table IV

Comparison of Growth on Diets with Different Percentages of Skimmed Milk

Powder as Source of Vitamin B

Percentage of milk powder in diet	Number of rats	Average gain G.	Probable error ^a	Increase over pre- ceding diet G.	Probable errorb	Coeffi- cient of variation in gains	Food eaten G.
20	11	54	± 5.7			52	348
25	11	106	± 6.6	52	± 8.7	31	441
30	11	133	± 5.4	27	± 8.5	20	511
a C 37	a . c H	-1-1- TIT					

^a See Note ^a of Table III.

The data summarized in Table IV illustrate well certain relationships usually found in vitamin experiments of this general type. Actual magnitude of the probable error of the average gain remains about the same as the gain increases with increased proportion of vitamin in the diet. Also the difference in gain in passing from diet to diet is considerably larger between 20 and 25, than between 25 and 30% of milk powder in the diet, yet the actual magnitude of the probable error of the two differences is about the same. The coefficient of variation is greatest for the diet containing (of those here compared) the smallest amount of vitamin and becomes less as the vitamin intake approaches the optimum. This is in accordance with the general experience of this Laboratory, that on diets permitting some growth but at a distinctly subnormal rate, individual variations are apt to be larger than on normal diet; and as the partially adequate diet is brought toward the optimum the rate of growth becomes both more rapid and more uniform. Certain observations in this Laboratory indicate further that as the diet is enriched in growth-promoting substances beyond the quantity or concentration required for optimum results individual variations again tend to increase, but we are not yet ready to generalize on this latter point.

The natural increase in total food intake with increasing rate of growth adds to the difficulty of interpreting growth rates quantitatively in terms of vitamin intake alone.

Effect of Heating at 100° upon Vitamin B in Milk in the Dry and Fluid States.—Dry heating was carried out by spreading the milk powder in a layer about 1 cm. deep in a flat-bottomed dish and heating in a constant-temperature oven, the temperature taken by means of a thermometer extending into the dry milk. When milk powder which had been heated for

^b See Note ^b of Table III.

^e "Coefficient of variation" = $\frac{\text{Standard Deviation}}{\text{Mean}} \times 100.$

6, 24 or 48 hours at 100° in the dry state, with free access of air, was substituted for the unheated dry milk, no effect of the heating could be detected, from the results as shown in Table V and in Fig. 2, Part 2.

TABLE V Comparison of Diets Containing 25 Per cent. of Skimmed Milk Powder, UNHEATED OR HEATED AT 100° Experiments with 15 rats

Time of heating of milk powder Hours	Average gai in weight in eight weeks G.	Probable error ^a	Difference from those receiving unheated milk G.	Probable errorb	Coefficient of variation in gainse	Average food intake G.
Unheated	84	± 5.0			34	520
6	88	± 5.0	4	± 7.1	33	511
24	87	± 3.0	3	± 5.8	20	506
48	82	± 4.2	2	± 6.5	29	455

For Notes a, b and c, see Tables III and IV.

Examination of the data in Table V shows plainly that the small differences in average gains on the heated and unheated milk powder are not significant; nor do the coefficients of variation or the data of food intake reveal any differences attributable to the heating of the milk. In view of the fact that the milk was the sole source of vitamin B and was fed at a level at which decrease of the vitamin B intake results in decrease of gain in weight, the results constitute strong evidence that the dry heating at 100° as here described caused no appreciable destruction of vitamin B. even when continued for 24 to 48 hours.

In another series of experiments the heated milk was fed separately from the basal diet, and in this series was also included the study of milk heated for 6 hours at 100° in fluid form, that is, in the presence of 9 to 10 parts by weight of water to 1 part of the skimmed milk solids. The results of the tests of the milk thus heated together with parallel tests on the same milk unheated and heated for 6 and 48 hours in the dry state are shown in Table VI. (Tests with milk heated dry for 24 hours were rejected because of accidental irregularities.)

TABLE VI Comparison of Tests with Milk as Source of Vitamin B, Unheated and Heated IN DRY OR IN FLUID FORM Experiments with 10 rats. Basal Diet 107.8 cc. of milk daily

Heat treat- ment of milk Hours at °C.	Average gain in weight in 8 weeks G.	Probable error ^a	Difference from that with un- heated milk G.	Probable error	Coeffi- cient of vari- ation of gains	Average food intake G.
Unheated	42	± 3.0	• •		33	283
6 100 (dry)	42	± 2.6	0	± 4.0	29	276
48 100 (dry)	37	±1.8	5	± 3.5	22	270
6 100 (wet)	6	± 1.6	36	±3.4	126	199

For Notes a, b and c, see Tables III and IV.

Here there was plainly no appreciable destruction of vitamin B in heating the milk powder dry for 6 hours at 100°, and probably no significant result when the same heating was continued for 48 hours. The animals receiving, as their sole source of vitamin B, the milk which had been heated 6 hours at 100°, wet, made distinctly lower average gains but showed much greater variability and a much lower average food intake. The average-weight curve for the rats receiving 8 cc. of milk thus heated approximates that of those receiving 6 cc. of unheated milk, so that if the difference due to heating the milk can be attributed wholly to destruction of vitamin B, the results would indicate a heat destruction of about $^{1}/_{4}$ of the vitamin B, as the result of heating for 6 hours in water at 100°. (The heating was carried out in thin-walled flasks immersed in briskly boiling water. A thermometer standing directly in the milk registered 99.5° to 99.8°.)

Thus there appears to have been an appreciable destruction in 6 hours' heating at 100° in water while there was no appreciable destruction in heating at 100° even up to 48 hours when the milk was heated in the dry state. Any seasonal differences in the growth of rats, and possible seasonal variations in the vitamin B content of milk, are eliminated here because all comparative tests were carried out simultaneously using milk powder from the same lot, and as previously explained the rats were all of exactly known age and relationship and were so distributed in the different tests that comparisons were nearly always with litter-controls.

Summary and Conclusions

A quantitative method for the determination of relative amounts of vitamin B by means of rat-growth experiments is described, and the known factors affecting the accuracy of the results of such experiments are discussed.

The data presented are representative of the work as a whole which comprised 11 series of experiments with a total of 38 variations of the experimental diet and included over 600 quantitative records of the food and growth of young rats.

The experiments were made upon rats of known age and relationship, the experimental period covering the fifth to the twelfth weeks of the rat's age, inclusive. It was found that the diet of the mothers from which the young rats are taken for experiment is a factor which must be kept uniform if results are to be as strictly quantitative as is possible.

Basal diets are described which are believed to be free from vitamin B and which are shown by numerous and rigorous tests to furnish practically optimum amounts of all other nutrients required by rats, the complete salt mixture of Osborne and Mendel being here considered as a unit.

The quantities of milk selected as most advantageous to feed in order to detect possible reduction in vitamin B content on heating were 0.8

g. of dry or 8 cc. of fluid skimmed milk per rat per day when fed separately from the basal ration, or 25% of the total food mixture when the skimmed milk powder was mixed with the basal diet.

By feeding the diets described to experimental animals of suitable age and size and sufficiently matched as to nutritional history and litter controls, it is believed to be possible, when dealing with averages of ten or more rats on each diet, to detect a diminution certainly of 25% and probably of 15% in the vitamin B content of the food tested.

There was no evidence of any measurable diminution of vitamin B in milk powder heated dry with free access of air at 100° even when this heating was continued for 48 hours. When the milk was heated in the fluid state for 6 hours at 100° there was an apparent diminution in its vitamin B content; probably about $^{1}/_{4}$ of the vitamin was thus destroyed. Vitamin B in the form in which it exists in milk is, therefore, comparatively stable to heating at 100° in the dry state, but less stable when heated at the same temperature in water solution.

NEW YORK, N. Y.

[Contribution from the Department of Chemistry, Columbia University, No. 425]

A QUANTITATIVE STUDY OF THE DESTRUCTION OF VITAMIN B BY HEAT

By H. C. Sherman and M. R. Grose Received August 6, 1923

In the study of vitamins the property of thermostability bears important relations both to the behavior of the vitamin in attempts to isolate it and to the conservation of the vitamin values of foods. Hence, statements regarding this property are frequently met, but most of the work which has been done to determine the effect of heating upon vitamins A and B has been qualitative, or little more than qualitative, in nature.

Building upon the work described in the two preceding papers^{1,2} we have attempted in the experiments here recorded to establish a quantitative relation between temperature and the rate of destruction by heat of vitamin B, somewhat as had been done in the previous work of this Laboratory with vitamin C.^{3,4}

Vitamin B is more stable than vitamin C both toward heat and toward oxidation but its destruction by heat can be studied on the same general principle by the use of higher temperatures. Using tests of the amounts of food required to cure polyneuritis in fowls or pigeons as the measure of

¹ Sherman and Edgeworth, This Journal, 45, 2712 (1923).

² Sherman and Spohn, ibid., 45, 2719 (1923).

Sherman, LaMer and Campbell, Proc. Nat. Acad. of Sci., 7, 279 (1921).

^{*}LaMer, Campbell and Sherman, This Journal, 44, 172 (1922).

vitamin B content, Chick and Hume reported $^{5.67}$ results which have been widely quoted as indicating that vitamin B is stable at 100° but rapidly destroyed at temperatures around 120° . This would seem to imply, chemically, a marked increase in the temperature coefficient of the process of heat destruction in the neighborhood of 120° and, nutritionally, a marked diminution of vitamin B value in foods which have been subjected to the temperatures commonly used in processing canned goods as compared with those which have been heated only to the ordinary cooking temperature of about 100° . For both of these reasons and also because the behavior on heating constitutes an interesting point of comparison of vitamins with enzymes, the present investigation was undertaken with the general plan of determining the percentage destruction of vitamin B when heated in solution for four hours at 100° , 110° , 120° and 130° at the hydrogenion concentration equivalent to PH 4.3.

Methods and Materials Employed

For reasons explained in previous papers from this Laboratory^{1,2} we have employed the rat-growth method for the detection and measurement of any diminution of vitamin B which might result from destruction by heat. Young rats of an initial age of 4 weeks were used and the experimental period was continued for 8 weeks. The initial weights of individual rats were usually between 40 and 55 g. The precautions developed in the work of Sherman and Spohn² were observed in the selection of animals of sufficient uniformity and the arrangement of litter-controls. The same basal diet was also employed, namely, purified casein, 18%; butter fat, 8%; cod liver oil, 2%; Osborne and Mendel salt mixture, \$ 4%; starch, 68%. This basal diet was given freely, the food which furnished the vitamin B being always fed separately. All experimental animals were kept in individual cages having raised floors of wire screen so that the animals did not have access to their excreta. The construction and the frequent cleaning of the cages both served as precautions against the possibility of the animals obtaining any significant amount of vitamin from their own urine or feces. No bedding was used and the technique of the handling of the animals was as previously described.2

The juice of canned tomatoes was selected as the source of vitamin B in these experiments. Osborne and Mendel have shown⁹ that tomatoes are a rich source of vitamin B. There is every reason to suppose that canned tomatoes of a given brand will be fairly constant in this respect, and the use of this material makes the present work on vitamin B directly

- 5 Chick and Hume, Proc. Royal Soc., 90B, 60 (1917).
- 6 Chick and Hume, Trans. Soc. Trop. Med. Hyg., 10, 141 (1917).
- ⁷ Chick and Hume, J. Roy. Army Med. Corps, 29, 121 (1917).
- 8 Osborne and Mendel, J. Biol. Chem., 37, 572 (1919).
- 9 Osborne and Mendel, ibid., 39, 29 (1919).

comparable in all respects with our previous work on vitamin C.^{3,4} The canned tomatoes used in this study were all of the same brand. They were purchased as needed and in the course of the work the products of two seasons were used. We encountered no indication of material variation in the vitamin content of the canned tomatoes as purchased. In preparing the juice for feeding, either with or without heat treatment, the contents of the can was first thrown on cheese cloth and the juice separated from the bulk of the pulp by suction and pressure. The resulting juice was then passed through filter paper, yielding a light yellow liquid, clear or slightly opalescent, which yielded a slight coagulum when boiled, and a little carbonized material at 130°.

The heating at 100° was carried out in Erlenmeyer flasks immersed to the necks in a bath of boiling water heated by live steam. Loosely fitting glass stoppers with flanges that rested on the tops of the flasks rendered the evaporation negligible. Tests showed that such an arrangement gave a temperature within the flask about 0.2° lower than that of the boiling water without.

For the three higher temperatures a steam-heated autoclave was employed, the juice being contained in large Erlenmeyer flasks, closed with inverted beakers. For each heating the pressure was rapidly increased until the gage indicated that the desired temperature had been reached. The exhaust was then adjusted and the whole held at constant pressure for 4 hours, measured from the time of turning on the steam to the time of turning it off. The air was always blown out of the autoclave carefully in order that the pressure-temperature relation, as expressed on the gage, should not be in error. The accuracy of the temperature control was checked by readings of a thermometer inserted in the well of the autoclave. It was not difficult to regulate the autoclave so that the variations were not greater than 1° on either side of the desired temperature. Both the heated and the unheated portions of juice were consumed readily by the experimental animals. The "daily" doses were fed for six days each week.

A series of over 100 experiments, each involving the feeding of an experimental animal for eight weeks, was devoted to the quantitative determination of the relation between the amount of unheated tomato juice fed daily as sole source of vitamin B and the resulting gain or loss of weight during the experimental period of eight weeks. It was found that the most regular results were obtained at a level of vitamin intake which resulted in little or no net gain in body weight during the eight weeks of the experiment. This is usually 4 or 5 cc. of tomato juice per day depending upon the initial weight of the rat. The animals used in the series of experiments represented in Fig. 1 averaged somewhat larger than those used in the subsequent series. Because of the greater regularity of results in the region

of maintenance or of only slight gain, this was adopted as the basis of comparison to be used in the study of the effects of heating in this investigation, the experimental method thus differing slightly at this point from that employed in the preceding investigation.² In the main series of experiments to determine the effects of heating, 4 cc. per day of unheated juice was fed to the "positive control" animals, and different doses of the heated juices were fed to other animals from the same litter as the control to determine what amount of heated juice was equivalent in vitamin B content to 4 cc. of unheated juice.

Experimental Results

Unheated Tomato Juice.—Various quantities of unheated tomato juice up to 14 cc. were fed, but few experiments were made with more than 10 cc. as this was about as much as the animals would readily consume. The

larger amounts also tended to diminish the consumption of solid food, so that with quantities greater than 8 cc. the growth, although still below normal, did not increase in proportion to the increased vitamin intake. The average-weight curves of the rats receiving daily doses of 0, 2, 4, 5, 6, 7, 8, 9 and 10 cc. of unheated juice are shown in Fig. 1 and the average initial eight weeks of experimental feeding are given in Table I.

Heated Tomato Juice.-The effect of heating for and 130° was studied by means of feeding experi-

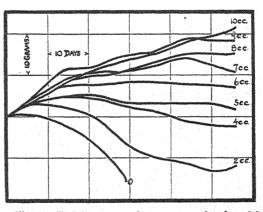


Fig. 1.-Weight curves of young rats showing the weights and total gain or effect of graduated doses of vitamin B in the form of loss in weight during the unheated tomato juice. Rats shown in curve marked O received the basal diet only, while those whose averages are shown by the other curves received this ration supplemented by daily doses of 2 cc. to 10 cc. of the unheated tomato juice as indicated on the curve. Table I shows the number and the average initial 4 hours at 100°, 110°, 120° weight and gain in weight of each group. The curves in this and following figures cover an experimental period of eight weeks

ments employing a total of about 50 animals for testing each temperature and varying the doses of the heated juices over a considerable range until the amount equivalent to 4 cc. (or to 5 or 6 cc.) of unheated juice had been approximated and then the experiment was repeated with doses at this level until averages establishing the equivalent quantities with sufficient precision were obtained.

Table I

Effects of Different Doses of Unheated Tomato Juice as Sole Source of Vitamin B

Amount of juice fed daily Cc.	Number of rats	Average initial weight G.	Gain in weight in 8 weeks G.	Probable error ¹⁰
10	10	55	21.4	± 1.1
9	5	58	18.2	± 3.4
8	10	53	15.3	± 2.1
7	7	45	10.7	± 2.6
6	21	48	7.0	± 0.2
5	11	42	1.6	± 1.4
4	25	48	- 2.2	± 0.9
2	6	54	-12.0	± 1.1
0	22	47	$(-16.0)^a$	$(\pm 0.8)^a$

[&]quot;The rats receiving none of the juice and whose food intake therefore was presumably entirely devoid of vitamin B showed an average survival period of 29 days and an average weight at death of 31 g.

Tables II, III, IV and V summarize the initial weights, food intakes and net changes in weight of those individual rats whose records are used in drawing the final averages. The left half of each table gives the record of the "positive controls" or rats receiving the unheated juice, while opposite these in the right half of the tables are given the records of the comparison animals receiving the heated juices, the two animals thus directly compared being always from the same litter. In this way physio-

Table II Experiments with Tomato Juice Unheated and Heated for Four Hours at $100\,^\circ$

		Rats fed unh Initial	eated doses Food			Rats fed he Initial	eated doses Food	
	Dose Cc.	weight G.	intake G.	Gain G.	Dose Cc.	weight G.	intake G.	Gain G.
	4	52	268	-10	5	51	257	- 3
	4	44	226	- 1	5	53	232	- 7
	4	23	205	11	5	23	179	+ 9
	4	44	219	2	5	45	227	- 7
	4	37	215	4	5	32	171	6
	4	40	211	4	5	40	217	4
	4	31	213	14	5	31	231	9
	4	43	201	3	5	38	223	10
Av.				+ 3.4				+ 2.6
	6	39	234	9	7	40	230	5
	6	58	356	13	7	43	299	6
	6	56	252	12	7	48	246	7
	6	47	223	5	8	49	207	6
	6	45	215	13	8	45	220	13
	4	42	252	- 4	6	38	229	1
Tot	al							
Av.	4.	743	235	+ 5.4	5.9	41	227	+ 4.2

¹⁶ Computed according to the classical method as described, for example, by Jevons, "Principles of Science," The MacMillan Co., New York and London, 1905, p. 387.

logical variation from litter to litter is excluded as a source of error in the comparison of the average results.

In case a test animal died during the experimental period neither its record nor that of its direct control is included in the averages. Such premature deaths were somewhat more frequent among the rats getting the more highly heated juices but did not constitute an important factor in any case.

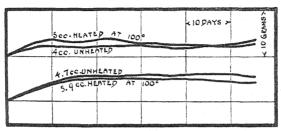


Fig. 2.—The upper curves show weights of rats receiving 4 cc. of unheated tomato juice in comparison with 5 cc. heated for 4 hours at 100°. The lower pair of curves represents the rats of Table II taken as a whole, and receiving an average dose of 4.7 cc. of unheated juice in comparison with 5.9 cc. heated for 4 hours at 100°

Of Tables II, III and V, each includes (1) a number of tests at a fixed ratio of dosage, (2) additional tests at varying ratios which latter are grouped together in the lower part of the table. Averages with or without these latter tests lead to the same conclusions. Feeling it somewhat safer in

TABLE III

EXPERIMENTS WITH TOMATO JUICE UNHEATED, AND HEATED FOR FOUR HOURS AT 110°

Rats fed unheated doses Rats fed heated doses

Dose Cc.	Initial weight G.	Food intake G.	Gain G,	Dose Cc.	Initial weight G.	Food intake G.	Gain G.
4	38	189	- 3	6	39	221	- 2
4	44	193	-13	6	46	215	-10
4	51	274	2	6	50	259	– 5
4	62	230	- 4	6	55	263	- 3
4	44	224	4	6	38	212	6
. 4	40	214	2	6	37	243	- 1
4	46	245	0	6	47	274	1
4	23	205	11	6	26	181	13
4	31	213	14	6	32	211	11
4	43	201	3	6	45	234	6
Av.			+ 1.6				+ 1.6
5	,49	230	- 1	6	49	253	- 4
4	51	263	- 2	7	54	252	-11
4	38	204	- 1	7	36	189	5
4	35	192	3	5	42	171	- 5
6	36	258	15	8	48	289	9
4	30	182	3	7	26	219	5
Total							
Av. 4.2	42	220	+ 1.8	6.3	42	230	+ 0.9

general to use the data of as many individuals as possible, we have made use chiefly of the "total average" from each table. In Fig. 2 are shown the

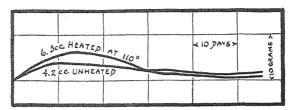


Fig. 3.—Weight curves of rats receiving an average dose of 4.2 cc. of unheated tomato juice in comparison with those receiving an average dose of 6.3 cc. heated for 4 hours at 110°

weight curves both of the averages of the rats receiving 4 cc. of unheated and 5 cc. of heated juices, respectively, and also the averages for all cases

Table IV

Experiments with Tomato Juice Unheated, and Heated for Four Hours at 120°

Ra	ts fed unhe		es		Rats fed h		S
Dose Cc.	Initial weight G	Food intake G.	Gain G.	Dose Cc.	Initial weight G.	Food intake G.	Gain G.
4	38	204	- 1	8	35	200	12
4	44	219	2	8	48	213	1
4	40	211	4	8	28	214	13
4	57	308	-12	8	57	254	-12
4	37	215	4	8	30	161	3
4	25	200	8	8	25	183	7
4	51	263	- 2	8	56	227	-11
4	50	250	- 4	8	65	287	- 3
4	45	254	0	7	37	223	- 1
4	46	245	0	7	45	235	- 5
4	23	205	11	7	26	202	13
4	40	211	4	7	38	208	10
4	43	201	3	7	47	229	0
Total							
Av. 4	41	230	+ 1.3	7.6	41	219	+2.1

in the table. Figs. 3, 4 and 5 show composite weight-curves for all the animals included in Tables III, IV and V, respectively.

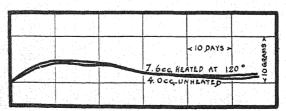


Fig. 4.—Weight curves of rats receiving 4 cc. of unheated tomato juice in comparison with those receiving an average dose of 7.6 cc. heated for 4 hours at 120°

 $\label{table V} \textbf{Experiments with Tomato Juice Unheated and Heated for Four Hours at 130°}$

Dose Cc.	Rats fed un Initial weight G.	heated dose Food intake G.	Gain G.	Dose Cc.	Rats fed he Initial weight G.	eated dose Food intake G.	s Gain G.
4	38	204	- 1	9	36	202	2
4	44	219	2	9	42	267	7
4	23	203	11	9	27	171	8
4	57	308	-12	9	47	229	- 7
4	33	222	3	9	35	177	- 5
Av.			+ 0.6				+ 1.0
4	37	204	- 1	10	40	223	7
4	32	205	- 2	12	29	187	7
4	43	201	3	8	48	175	-11
4	44	226	- 1	7	59	229	- 7
4	43	225	- 1	7	52	229	-12
Total							
Av. 4	. 39	222	+ 0.1	8.9	41	209	- 1.1

It will be seen that throughout the four series of experiments summarized in Tables II to V, each experimental animal is paralleled by a litter control, and in each series the average initial weights of experimental and control animals are practically equal. This being the case, it has not seemed

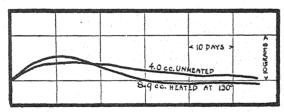


Fig. 5.—Weight curves of rats receiving 4 cc. of unheated tomato juice in comparison with those receiving an average dose of 8.9 cc. heated for 4 hours at 130°

essential to the purpose of this paper to discuss the relation of dosage to initial weights of individual experimental animals. From the data given this can easily be computed by any reader who desires to do so.

Discussion and Interpretation

The Percentage of Vitamin B Destroyed.—In each of the four tables given above the gain in weight of the animals receiving the heated juice is approximately the same as that of the positive controls. The curves of these sets of animals given in Figs. 2 to 5 further show that the two sets of animals closely parallel each other throughout the experimental period. It may, therefore, be concluded that the average doses of heated and unheated juice as given in each table are essentially equal in vitamin content. This being the case, the percentage of destruction by 4 hours' heating can be derived directly from the data of each table as follows.

Ce.	Temperature of heating °C.	Equivalent to unheated juice Cc.	Destruction
5.0	100	4.0	20
5.9	100	4.7	20
6.0	110	4.0	33
6.3	110	4.2	33
7.6	120	4.0	47
8.9	130	4.0	55

The data as obtained and employed in these tables are thought to involve a minimum of error, and the method of arriving at the percentage of destruction is both direct and simple.

In deriving the figures for destruction just given, the curves for the two sets of animals have been taken as substantially identical. If desired, one may compute them to coincidence in a comparatively simple manner, but it is open to question whether figures so obtained are of any higher order of precision.

To do this it is necessary only to compute the change required in the unheated doses to bring the two comparison curves into coincidence at the termination of the eight-weeks period. This is done by using the relation established between growth and unheated juice in the experiments summarized in Table I. The method of computing may be illustrated using the figures from the table for 100°. Here the positive controls give a curve terminating 1.2 g. (5.4–4.2) above that for the animals receiving heated juice; or, better, taking only those receiving doses of 4 as against 5 cc., the difference is 0.8 g. Since a difference of 1 g. in weight at the end of the eight weeks corresponds to about 0.25 cc. of unheated juice per day, the curves may be brought into coincidence by reducing the unheated dose of the positive controls from 4.7 to 4.4 cc. as against 5.9 cc., or better to 3.8 cc. against 5 cc., and the destruction at 100° becomes 24%. Carrying out similar computations for the averages of Tables IV and V gives indication of a destruction of 45% at 120° and 58% at 130°.

For destruction at 110°, the best data are probably those of the upper groups only in Table III which show exact agreement at 4 as compared with 6 cc. or a destruction of 33%.

Hence, according as we take the average data as they stand or the revised data resulting from the assumptions and calculations just explained, we obtain the two following series of estimates for heat destruction of vitamin B in 4 hours at the temperatures stated: at 100° , 20% or 24%; at 110° , 33%; at 120° , 47% or 45%; at 130° , 55% or 58%. The temperature coefficients computed for the three 10° intervals are:

```
Q_{10} (100-110^{\circ}) 33/20 = 1.6 \text{ or } 33/24 = 1.4
Q_{10} (110-120^{\circ}) 47/33 = 1.4 \text{ or } 45/33 = 1.3
Q_{10} (120-130^{\circ}) 55/47 = 1.2 \text{ or } 58/45 = 1.3
Q_{10} (Av. 100-130^{\circ}) 1.4 \text{ or } 1.33
```

Viewed from any standpoint the results plainly show that about $^{1}/_{5}$ to $^{1}/_{4}$ of the vitamin is destroyed by being heated for 4 hours at 100° in slightly acid medium and that (the other conditions remaining the same) about $^{1}/_{3}$ is destroyed at 110° , slightly less than $^{1}/_{2}$ at 120° , slightly more than $^{1}/_{2}$ at 130° . The temperature coefficient of the destructive process is distinctly lower than that of most chemical reactions, resembling in this respect that of vitamin C, and there is no rapid rise in the rate of destruction at temperatures around 120° as had been inferred from earlier work.

The low temperature coefficient of destruction by heat makes it improbable that the vitamin is an unstable protein, and inappropriate to group it with enzymes since the typical enzymes which have been studied in this respect have shown rates of destruction by heat with high temperature coefficients up to the point at which the enzymic activity was entirely destroyed.

Summary and Conclusions

The effect of 4 hours' heating upon vitamin B of tomato juice has been investigated at 10° intervals over the range of 100° to 130° using the growth of young rats during an experimental period of eight weeks as a measure of vitamin B content.

For this purpose a dosage giving approximate maintenance has been found to be the best level of feeding. The disturbing factors are thus minimized and the sensitivity of the method is apparently at a maximum.

The results show that when heated at a temperature of 100° for 4 hours in slightly acid medium there is an appreciable destruction of vitamin B, a fact in agreement with previous results obtained in this Laboratory, using milk in the liquid state as the source of vitamin B.

That this destruction is due to the effect of the hot water upon the vitamin, and not to the possible presence of dissolved air is indicated by the fact that much longer heating at 100° in the dry state with free access of air resulted in no appreciable destruction of vitamin B. (Experiments of Sherman and Spohn.)

The average figures for destruction of vitamin B in tomato juice, derived directly by determining the size of heated doses at each temperature necessary to give weight curves approximately coinciding with those of positive controls fed 4 cc. of unheated juice are for a period of 4 hours' heating, as follows: at 100°, 20%; at 110°, 33%; at 120°, 47%; at 130°; 55%.

By a further simple mathematical computation bringing the comparison curves into exact coincidence, the following slightly different figures have been obtained: at 100°, 24%; at 110°, 33%; at 120°, 45%; at 130°, 58%.

These figures establish a low temperature coefficient of heat destruction as one of the characteristics of vitamin B, a property possessed also by vitamin C as shown by the previous experiments of Delf and of LaMer,

Campbell and Sherman. For an increase of 10° in the temperature range of 100° to 130°, the rate of heat destruction of vitamin B in solutions such as here studied is increased only 1.3–1.4-fold, as compared with a 2-fold increase in most chemical reactions.

In the work here presented there was no indication of an increased temperature coefficient of heat destruction at temperatures around 120°. We find no evidence of any departure from the orderly course of a chemical reaction under the accelerating influence of heat but with a less than average temperature coefficient.

In this respect the heat destruction of the vitamin is in marked contrast with the heat coagulation of typical proteins and with the heat destruction of such typical enzymes as have been investigated.

As previously suggested in the case of vitamin C, the low temperature coefficient of the heat destruction of vitamin B may perhaps be due to the reaction being one which involves two phases of a heterogeneous system, the vitamin being in combination with or adsorbed upon colloidal material rather than in true solution in the hot water by which it is destroyed.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SYNTHESIS OF A NEW BICYCLIC NITROGEN RING. ISOGRANATANINE DERIVATIVES. PREPARATION OF AN ISOMER OF HOMOCOCAINE

By S. M. McElvain¹ with Roger Adams

RECEIVED AUGUST 9, 1923

Molecules containing bicyclic rings of an aliphatic character with a nitrogen atom in common occur in many of the natural alkaloids. Of these the most important are dihydro-nortropidine (I), quinuclidine (II), and granatanine (III), the basic nuclei of cocaine, quinine and pseudo-pelletierine respectively. The method described in this communication has been developed for the preparation of derivatives of a nucleus isomeric with granatanine, to which has been given the name isogranatanine (IV); a new ring resembling quinuclidine fairly closely.

¹ This communication is an abstract of a thesis submitted by S. M. McElvain in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

A nomenclature for the derivatives of this ring exactly analogous to that given granatanine compounds² has been adopted.

The syntheses of compounds containing rings of this character are very limited in number. Willstätter³ has prepared dihydro-nortropidine compounds in two ways, the first represented by the formation of bromotropane methyl ammonium bromide by heating δ -4-dimethylamino-cycloheptene bromide,

$$\begin{array}{c} N(CH_3)_2 \\ CH_2-\overset{!}{C}H-CH_2 \\ CH_2 \\ CH_2 \\ CH_2-CHBr-CHBr \end{array} \longrightarrow \begin{array}{c} CH_2-\overset{!}{C}H-\overset{!}{C}H_2 \\ (CH_3)_2NBr \\ CH_2-\overset{!}{C}H-\overset{!}{C}HBr \\ \end{array}$$

and the second by the formation of ethyl tropinone-carboxylate⁴ by an internal aceto-acetic ester condensation from pyrrolidine diacetic ester.

A study of quinine has led to a third method for the preparation of a bicyclic ring. This is illustrated by the formation of quininone⁵ by the action of alkali on N-bromoquinicine. In this reaction a 4-(β -keto-ethyl)piperidine, upon treatment with sodium hypobromite and alkali, gives first a 4-(β -keto-ethyl)piperidine-N-bromide which then loses hydrogen bromide to give a bicyclic ring, the hydrogen of the hydrogen bromide coming from the carbon atom adjacent to the ketone group.

$$\begin{array}{c|cccc} CH_2-CH-CH_2-CH_2COR & CH_2-CH-CH_2 \\ & CH_2 & & CH_2 \\ & CH_2 & & CH_2 \\ & CH_2 & & CH_2 \\ & CH_2 & & CH_2-N-CH-COR \\ \end{array}$$

Still another method has appeared, but it is doubtful whether it can be applied as generally as those methods illustrated by the examples just given. Robinson⁶ has prepared tropinone in 42% yields by the action of succinaldehyde, methyl amine and calcium acetone-dicarboxylate.

The method employed for the preparation of isogranatanine derivatives has involved an internal aceto-acetic ester condensation. Ethyl β -(3-

- ² Meyer and Jacobson, "Lehrbuch der organischen chemie," Walter De Gruyter and Co., 1920, vol. 2, sec. III, p. 1077.
 - ³ Willstätter, Ber., 34, 129 (1901).
 - 4 Willstätter and Bommer, Ann., 422, 15 (1921).
 - ⁵ Rabe and Kindler, Ber., 51, 466 (1918).
 - 'Robinson, J. Chem. Soc., 111, 762 (1917).

carbo-ethoxy-piperidino)propionate has been converted by means of sodium in xylene into ethyl isogranatonine-carboxylate.

With this substance available it is obvious that, by employing well-known reactions, isogranatanine and numerous other derivatives can be produced.

The general properties of ethyl isogranatonine-carboxylate are of interest. The free base is a colorless liquid, the hydrochloride a white solid. Both Ruzicka⁷ and Willstätter⁸ have studied amino β-ketonic esters of an analogous type and the latter has mentioned that they were thick oils which could not be purified because of the fact that even on standing in the cold they showed a tendency toward isomerization with the formation of a crystalline inner salt. This ketonic ester also is a thick oil which on standing in the cold gradually crystallizes. It has been found, however, that the ester can be purified if the proper conditions are used and it is probable that in a similar way the compounds made by these previous investigators could also be purified. The bath must be heated to considerably above the boiling point of the ester before the distilling flask containing it is immersed in the bath. In this way 60% of the original keto ester distils as a clear, colorless liquid while about 40% isomerizes or decomposes and remains behind in the flask. The distilled product is apparently perfectly stable and has been kept for several months without showing the slightest tendency to crystallize. The crystalline isomerization product can be readily obtained by dissolving the crude keto ester in ether and allowing the solution to stand; white crystals gradually deposit which have the solubility in organic solvents not of a base but of an ammonium compound. Undoubtedly an inner salt formation has taken place, as represented by Formula VII. The keto ester gives a characteristic coloration with ferric chloride, thus making it possible to distinguish it from its isomer, VIII, none of which, however, could be isolated from the reaction mixture.

8 Ref. 4, p. 30.

⁷ Ruzicka and others, Helvetica Chim. Acta, 3, 817 (1920); 5, 717 (1922).

The yields in this synthesis were low, as has also been true in all syntheses of similar types of compounds previously described. This is unquestionably due to the fact that the condensation may take place in several ways, especially with the formation of several types of dimolecular compounds. Moreover, unlike the compounds used for analogous internal condensations, which are symmetrical, the starting material in this reaction is unsymmetrical in nature. In spite of the low yields, a study of the ethyl isogranatonine carboxylate and its derivatives was rendered possible because of the ease with which the starting material, ethyl β -(3-carbo-ethoxy-piperidino) propionate, could be made in quantity. This latter substance (V) is produced from nicotinic acid (pyridine-3-carboxylic acid) which is readily formed by the oxidation of nicotine with nitric acid. Since nicotine is now a cheap commercial product, nicotinic acid is an easily available substance for the organic chemist. By means of a platinum oxide catalyst described recently,9 nicotinic acid hydrochloride may be readily reduced in comparatively large quantities to nipecotic acid hydrochloride, the hexahydro derivative. This reduced product is esterified to ethyl nipecotate and the latter condensed in the usual way with ethyl β -chloropropionate to give ethyl β -(3-carbo-ethoxy-piperidino) propionate.

The ethyl nipecotate was also condensed with ethyl chloro-acetate to give ethyl (3-carbo-ethoxy-piperidino)acetate. This latter substance did not condense with sodium to give a bicyclic ring.

The particular isogranatanine derivative of which a study has been made is the hydrochloride of ethyl benzoyl-isogranatoline-carboxylate (X) formed by the benzoylation of the hydrochloride of the alcohol, ethyl isogranatoline-carboxylate (IX), obtained by the reduction of the hydrochloride of ethyl isogranatonine-carboxylate (VI). This benzoyl derivative is very closely related to cocaine in structure.

During the past 25 years the importance of cocaine has led to a thorough study of synthetic substitutes. The important members of this latter class which have been discovered do not contain an alicyclic ring and are comparatively simple compounds. A study of substances more closely related to cocaine has been neglected on account of the difficulty of preparation and of the purely theoretical value of such information. It has been shown that slight changes in the structure of the cocaine molecule

⁹ Voorhees and Adams, This Journal, 44, 1397 (1922). Carothers and Adams, ibid., 45, 1071 (1923). Adams and Shriner, ibid., 45, 2171 (1923).

modify the therapeutic effect materially. This can be seen by a comparison of cocaine with α -cocaine¹⁰ (XI) and eccaine¹¹ (XII).

 α -Cocaine has no anesthetic action, whereas eccaine is a more powerful anesthetic than cocaine and is considerably less toxic. In the production of these two latter substances, basic changes in the bicyclic nucleus of cocaine have not been effected; the groups attached to the nucleus have merely been rearranged and changed. Until now, no attempt to find the effect of changes in the nature of the bicyclic ring has been made. In ethyl benzoyl-isogranatoline-carboxylate the ring containing the groupings essential to anesthesia in the bicyclic ring is left intact and the second ring is changed. The similarity between homococaine (XIII) and ethyl benzoyl-isogranatoline-carboxylate (X), and the change that has been effected, may be seen by writing the formula of the latter in a slightly different form (XIV).

The carbon atoms numbered 1, 2 and 3 in homococaine are still present in the new compound, but are attached in a slightly different manner.

The pharmacological action of ethyl-benzoyl-isogranatoline-carboxylate hydrochloride was kindly tested by Mr. Carl Nielsen of the Abbott Laboratories, Chicago, Illinois. It was found that if a 1% solution was injected intravenously into rabbits at the rate of 1 cc. in 18 seconds, the average toxicity was about twice that of cocaine hydrochloride. By a similar procedure, by injecting subcutaneously, the toxicity appeared to be about five times that of cocaine hydrochloride.

A 2% solution was applied to a rabbit's cornea. This, however, did not produce complete anesthesia. Moreover, the solution appeared to be distinctly more irritating than a similar solution of cocaine hydrochloride though it was only very faintly acid in reaction. There was no sign of dilation of the pupil, as is noticed with cocaine hydrochloride.

In regard to the formation of ethyl benzoyl-isogranatoline-carboxylate, it may be mentioned that the ethyl isogranatoline-carboxylate hydro-

¹⁹ Willstätter, Ber., 29, 2216 (1896).

¹¹ Von Braun, Ber., 51, 235 (1918).

chloride was formed by the catalytic reduction of the keto ester hydrochloride by means of platinum oxide as a catalyst. Willstätter¹² found that the reduction of an analogous keto ester was accomplished conveniently by means of sodium amalgam but the yields were very low. The results in this investigation showed that sodium amalgam could also be used but not only was the yield low, but two stereoisomers were formed simultaneously. No such complication occurred in the catalytic reduction; it required, however, a long period of time and a large amount of platinum. The product formed in this latter way was the same as one of the two isomers obtained by the sodium amalgam reduction. Benzoylation of the ethyl isogranatoline-carboxylate could not be accomplished by means of benzoic anhydride in toluene. It was effected by the action of benzoyl chloride upon the hydrochloride of the ethyl isogranatoline-carboxylate at a moderately high temperature.

Experimental Part 13

Nicotinic Acid Nitrate (Pyridine-3-carboxylic Acid Nitrate).—In a 5-liter round-bottom flask was placed 4 kg. of c. p. concd. nitric acid (d. 1.42). To this was added in 25cc. portions 210 g. of 95% nicotine. The addition was made carefully in order to prevent local heating and consequent loss of material. After each addition of nicotine the flask was shaken in order to insure a homogeneous solution. The addition of the nicotine caused the temperature of the liquid to rise somewhat but not sufficiently to cause evolution of oxides of nitrogen. The flask was then placed on a steam cone under a hood. As the liquid became warmed a vigorous reaction set in and sufficient heat was evolved to cause the liquid to boil. The boiling ceased after about 1 hour, but the flask was allowed to stand on the steam cone for 10 hours, during which time there was a more or less continuous evolution of oxides of nitrogen.

The contents of the flask were then poured into an evaporating dish and evaporated to dryness on the steam cone. The purification which follows was best carried out with the product of two such runs as described above.

The nicotinic acid nitrate from two runs, after evaporation of most of the liquid, was transferred to a 1.5-liter beaker, 400 cc. of distilled water was added, and the mixture heated until complete solution resulted. As this solution cooled, the nicotinic acid nitrate separated as yellowish crystals. It contained one molecule of water of crystallization and melted at 190–192°. By recrystallization from water with bone black, it could be obtained almost white. The yield was 430–460 g. No more of the nitrate could be obtained from the filtrate.

Nicotinic acid salts have been prepared by a number of methods of which only three are practical for making them in any quantity. Fischer¹⁴ prepared 3-cyanopyridine by the fusion of the corresponding sulfonic acid with sodium cyanide and then hydrolyzed this compound to nicotinic acid. The second method is by the decomposition of quinolinic acid.¹⁵ The third is by the oxidation of nicotine with nitric acid, ¹⁶ with potassium per-

¹² Ref. 4, p. 32.

¹³ All melting points and boiling points herein given are corrected.

¹⁴ Fischer, Ber., 15, 63 (1882).

^{15 &}quot;Organic Chemical Reagents," University of Illinois Press, 1922, IV, p. 39.

^{16 (}a) Weidel, Ann., 165, 331 (1873). (b) Pictet, Chem. Zentr., 1898, 1, 677.

manganate, " and with chromic acid. " Since nicotine is a commercial product of sold at a comparatively low cost, this latter method is by far the best process. The details given above allow for its production on a comparatively large scale with cheap reagents.

Nicotinic Acid Hydrochloride.—The nicotinic acid nitrate, which did not necessarily have to be dried, was placed in a 3-liter flask and 1000 cc. of coned. hydrochloric acid (d., 1.2) was added. This mixture was heated on a steam cone as long as gas evolution continued (6-8 hours). The flask was then connected to a condenser and the liquid removed under diminshed pressure (17-100 mm.). The dry salt thus obtained was covered with 500 cc. more of concd. hydrochloric acid (d., 1.2) and heated on a steam cone for about 5 hours longer. This was also distilled off in a vacuum and the dry salt remaining transferred to a 2-liter beaker and dissolved in 400 cc. of distilled water. Heating nearly to the boiling point was necessary to effect solution. The solution was diluted to about 4 times its original volume with 95% alcohol, placed in an ice-bath and stirred vigorously in order to form fine crystals. The precipitated hydrochloride was filtered and air-dried. It was white or cream colored and weighed 245 to 250 g. The filtrate was evaporated to dryness and the residue dissolved in the smallest possible amount of boiling water, diluted with alcohol and precipitated as described above. The precipitate was usually a light straw color and weighed 65 to 70 g. From the filtrate of this crystallization 10 to 15 g. of the hydrochloride was recovered. The total yield from two runs was 315 to 325 g. (80-83% yield); m. p., 273-274°. The material could be obtained pure and white by one recrystallization from water with bone black.

Nicotinic acid hydrochloride^{16,17} has previously always been prepared from nicotinic acid by neutralization with hydrochloric acid, a procedure much more tedious than the one just described.

Nicotinic Acid.—This was best prepared by dissolving 160 g. of the hydrochloride in 300 cc. of water and adding slowly a solution of 53 g. of anhydrous sodium carbonate in 150 cc. of water. Free nicotinic acid precipitated out and was filtered off. By concentrating the filtrate and allowing it to crystallize, more of the acid was obtained. Nicotinic acid was best recrystallized from hot water. The yield in this preparation was from 117 to 120 g. (95–98%); m. p., 230–232°.

Nicotinic acid has previously been made from the silver salt by precipitation with hydrogen sulfide^{16a} or from the copper salt by a similar procedure.^{16b} There is no difficulty in obtaining it directly from the salts by the action of sodium carbonate; in fact, it could undoubtedly be prepared from the nitrate instead of the hydrochloride. The reason why a method from the nitrate was not used was that the nitrate varies in composition as regards water of crystallization, thus complicating the calculation for the exact amount of alkali needed. The hydrochloride has no water of crystallization.

Ethyl Nicotinate.—A mixture of 50 g. of nicotinic acid, or 65 g. of nicotinic acid hydrochloride, with 200 g. of thionyl chloride was refluxed until complete solution took place (2 hours). The excess thionyl chloride was recovered by distillation from a steam cone and the last traces removed in a vacuum. The flask, containing the crystalline residue of the acid chloride hydrochloride, was again fitted with a reflux condenser and 100 cc. of absolute alcohol was added through the condenser. After refluxing this mixture for 1 hour the excess alcohol was removed under diminished pressure. The remaining crystals were covered with 150 cc. of benzene and 20% sodium carbonate solution

¹⁷ Laiblin, Ber., 10, 2136 (1877); Ann., 196, 135 (1879).

¹⁸ Huber, Ann., 141, 271 (1867); Ber., 3, 849 (1870).

¹⁹ The nicotine used in this investigation was purchased from the Hall Tobacco Company, St. Louis, Missouri. It was 95% pure but by one fractionation could readily be obtained practically 100% pure. The commercial material, however, was perfectly satisfactory for the oxidation with nitric acid.

was added until the aqueous layer was alkaline (about 135 cc.). The benzene layer was separated, the benzene removed, and the ethyl nicotinate distilled under diminished pressure; b. p., 103–105° (5 mm.); yield, 52–55 g., or 85–90%.

The esters of nicotinic acid have been prepared previously by the action of nicotinic acid, ²⁰ alcohol and hydrogen chloride, or nicotinic acid, alcohol and sulfuric acid. ²¹ It is mentioned in a paper on the preparation of acid chlorides of pyridine-carboxylic acids that the esters may be made by the action of alcohols on these compounds²² but no experimental details are given. This last procedure was found to be by far the most satisfactory for giving consistent results.

Nipecotic Acid Hydrochloride.—To a solution of 50 g. of nicotinic acid hydrochloride in 125 cc. of water was added 1 g. of platinum oxide catalyst, made from c. p. chloroplatinic acid²³ of commerce and the mixture was reduced under 1.5 atmospheres' pressure. The reduction was complete in 24 hours when one reactivation was made about 10 hours after the hydrogenation was started. The same catalyst was used over again, but it was advisable to add 0.25 g. of fresh platinum oxide with each subsequent reduction of 50 g. portions of nicotinic acid hydrochloride. In this way it was possible to reduce 300 g. of nicotinic acid hydrochloride with 2.25 g. of catalyst in approximately 6 days, when one reactivation with air²⁴ was made about 10 hours after the beginning of each reduction. After the catalyst was filtered off, the water was removed under diminished pressure. The yield was quantitative. After one recrystallization from alcohol the product melted at 240–242°.

The melting points which have previously been found by Ladenberg²⁵ and Freudenberg²⁵ are, respectively, 239–240° and 240–241°. These agree with the melting point obtained in this research, showing unquestionably that Hess²⁷ did not use nicotinic acid in his investigation.

Nipecotic acid hydrochloride has been previously prepared by the reduction of nicotinic acid with sodium and alcohol,²⁵ by the reduction of quinolinic acid with sodium and amyl alcohol²⁸ and by the catalytic reduction with platinum black.²⁶ The platinum oxide catalyst has proved to be much more active than any of those previously used and is to be recommended when large amounts of this product are desired.

Ethyl Nipecotate.—The aqueous solution of nipecotic acid hydrochloride representing the reduction of three 50 g. portions of nicotinic acid hydrochloride, was placed in a 3-liter flask and the water removed completely under diminished pressure. The dry residue was covered with 1200 cc. of a 5–6% solution of hydrogen chloride in absolute alcohol. The solution thus obtained was refluxed for 12 hours. The alcohol was then removed in a vacuum until 500–600 cc. of solution remained, the solution cooled to 0–5°, and 200 cc. of ether added. The liquid was transferred to a 2-liter separatory funnel and shaken vigorously with 150 cc. of 30% sodium hydroxide solution. The aqueous

²⁰ Engler, Ber., 27, 1784 (1894). Pollak, Monatsh., 16, 46 (1895).

²¹ Camps, Arch. Pharm., 240, 354 (1902).

²² Meyer, Monatsh., 22, 113 (1901).

²³ The chloroplatinic acid was the c. P. grade purchased from the Mallinckrodt Chemical Company, St. Louis, Mo.

²⁴ It is probable that if oxygen under pressure had been used for reactivation of the platinum catalyst, the time necessary for the reduction would have been reduced considerably. This work was completed before it was found that oxygen under pressure was very much more efficient than air in the reactivation.

²⁵ Ladenberg, Ber., 25, 2768 (1892).

²⁶ Freudenberg, Ber., 51, 1668 (1918).

²⁷ Hess and Liebbrandt, Ber., 50, 385 (1917).

²⁸ Bésthorn, Ber., 28, 3151 (1895).

alkaline layer was withdrawn, and extracted twice more with 200cc. portions of ether. The ether was removed from the combined ether extracts, thus leaving an alcoholic solution of the ester from which the alcohol was best removed under diminished pressure. The remaining ester was distilled under diminished pressure. The yield was 103–110 g. (70-75%) of product boiling at $102-104^{\circ}$ (7 mm.). The ester was a colorless water-soluble liquid; d_{20}^{20} , 1.0121; $n_{\rm D}^{19}$, 1.4592.

Analyses. Subs., 0.6421, 0.7116: 41.68 cc., 45.87 cc. of 0.0969 N HCl. Calc. for $C_8H_{18}O_2N$: N, 8.92. Found: 8.80, 8.75.

Ethyl Nipecotate Hydrochloride.—The hydrochloride was prepared by the addition of hydrogen chloride to an ether solution of the free base. The ether was poured off and the precipitate dissolved in as small a quantity of hot 95% alcohol as possible. To this solution ether was added until a faint cloudiness appeared, and the solution was then placed in an ice-bath. Ethyl nipecotate hydrochloride crystallized from the solution in needles which melted at 110–111°. This hydrochloride was stable to alkali carbonates.

Analyses. Subs., 0.1840, 0.2065: AgCl, 0.1358, 0.1525. Calc. for $C_8H_{16}O_2NCl$: Cl, 18.35. Found: 18.25, 18.26.

Ethyl nipecotate was also prepared by the catalytic reduction of ethyl nicotinate hydrochloride in alcoholic solution and by the reduction of ethyl nicotinate in alcohol containing 2 molecules of acetic acid. The yields were not nearly so satisfactory as in the above procedure.

$$\begin{array}{c|c} CH_2-CHCO_2C_2H_5\\ & | \\ \\ Ethyl \ \ (3-Carbo-ethoxy-piperidino) acetate, \\ CH_2 \ CH_2 \ .--A \ solution \ of \\ & | \\ CH_2-N-CH_2CO_2CH_5 \end{array}$$

 $100~\rm g.$ of ethyl nipecotate in $500~\rm cc.$ of 95% alcohol in a 1-liter flask was treated with $80~\rm g.$ of ethyl chloro-acetate. The solution on shaking became warm. To this was added $80~\rm g.$ of finely powdered silver oxide and the mixture shaken at frequent intervals until a test portion of the supernatant liquid, after acidification with nitric acid, gave no appreciable test for chloride with silver nitrate. This required from 6 to 8 hours. The contents of the flask were then heated to boiling on a steam cone in order to coagulate the silver chloride precipitate. This precipitate was filtered off by suction and washed once with $100~\rm cc.$ of warm alcohol, while stirred in a beaker. The alcohol from the combined filtrates was removed under diminished pressure and the remaining ester distilled. It boiled at $147-149°~(5~\rm mm.)$; d_{20}^{20} , 1.0684; n_{10}^{10} , 1.4607; yield $120-125~\rm g.$, or 80-83%. It was colorless when freshly distilled but on standing slowly acquired a pale yellow tinge. It was insoluble in water, and solutions of its mineral acid salts were decomposed by alkali carbonates.

Analyses. Subs., 1.1630, 1.2830: 48.85, 52.80 cc. of 0.0969 N HCl. Calc. for $C_{19}H_{21}O_4N$: N, 5.76. Found: 5.71, 5.60.

Attempts were made to condense this ester into a bicyclic system by the use of sodium ethylate in benzene, and sodium in toluene, xylene and cymene. However, the ring formation could not be effected with any of these reagents and it was possible to recover from 60-80% of the unchanged diester from each attempted condensation.

ETHOXY-PIPERIDINO) ACETATE.—A mixture of 5 g. of ethyl (3-carbo-ethoxy piperidino)-acetate, 10 g. of barium hydroxide and 250 cc. of water was refluxed for 2 hours in a 500cc. Hask. The excess barium was removed from the hot solution by carbon dioxide and

filtration. To the filtrate was added dil. sulfuric acid until the remaining barium was just completely precipitated. This precipitate was filtered and to the resulting filtrate 10 g. of copper oxide powder was added. After the mixture had been refluxed for 1 hour and filtered, a deep blue solution of the copper salt of the acid was obtained. This solution was concentrated to a volume of about 25 cc. and allowed to cool. The copper salt of the acid crystallized in deep blue crystals. These were dissolved in 100 cc. of hot water and the copper was precipitated by hydrogen sulfide. The precipitated sulfide was removed by filtration and the filtrate evaporated to dryness on a steam cone. The residue after recrystallization from an alcohol-ether mixture formed white crystals and melted at 268–270° (with decomp.); yield, 2.5 g., or 65%.

From Nipecotic Acid Hydrochloride.—A mixture of 10 g. of nipecotic acid hydrochloride, 7 g. of chloro-acetic acid and 13 g. of sodium hydroxide was dissolved in 250 cc. of water and the solution stirred for 3 hours. Hydrochloric acid was then added until the reaction was acid to congo red and the solution evaporated to dryness under diminished pressure. The residue was treated with 200 cc. of hot 95% alcohol and the sodium chloride remaining was removed by filtration. From the filtrate the alcohol was removed under diminished pressure, leaving a yellowish amorphous residue. From this residue, the dibasic acid was isolated through the copper salt as described above; yield, 3.5–4.5 g., or 31–40%. This acid was identical with the one obtained by the hydrolysis of ethyl (3-carbo-ethoxy-piperidino)acetate.

Analyses. Subs., 0.7432, 0.6918: 40.35, 36.85 cc. of 0.0969 N HCl. Calc. for $C_8H_{18}O_4N$: N, 7.48. Found: 7.35, 7.22.

Ethyl (3-Carbo-ethoxy-piperidino)propionate (V). From Ethyl, Nipecotate,—A solution of 100 g, of ethyl nipecotate in 500 cc. of 95% alcohol was mixed with 90 g, of ethyl chloropropionate in a 1-liter round-bottom flask. The remainder of the procedure was exactly the same as that described for the preparation of the ethyl (3-carbo-ethoxy-piperidino)acetate. The product was a colorless, water-insoluble oil, boiling at 159–161° (5 mm.); $d_{\rm 20}^{20}$, 1.0452; $n_{\rm D}^{13}$, 1.4605; yield, 126-135 g., or 78-83%. As in the case of its lower homolog, aqueous solutions of its mineral acid salts were decomposed by alkali carbonates.

Analyses. Subs., 0.9790, 1.1891: 38.05, 46.93 cc. of 0.0969 N HCl. Calc. for $C_{18}H_{29}O_4N$: N, 5.45. Found: 5.29, 5.36.

From Nipecotic Acid Hydrochloride.—A mixture of 50 g. of nipecotic acid hydrochloride, 50 g. of β -chloropropionic acid and 65 g. of sodium hydroxide in 500 cc. of water was stirred for 3 hours at room temperature. After this time hydrochloric acid was added until the reaction was acid to congo red. The water was then removed from the solution under diminished pressure and the resultant salt residue treated with 500 cc. of hot 95% alcohol. The solution was filtered from the sodium chloride, placed in a 1-liter flask and evaporated to complete dryness under diminished pressure. The residue was esterified and the ester recovered by the same method as that described for the preparation of ethyl nipecotate from nipecotic acid hydrochloride; yield, 20–28 g., or 25–35%; b. p., 157–162° (5 mm.).

Ethyl Isogranatonine-carboxylate Hydrochloride (VI).—A mixture of 10 g. of freshly cut sodium and 100 cc. of xylene was placed in a 500cc. flask fitted with a ground-glass reflux condenser. The sodium was finely powdered by first heating it in the xylene to boiling and then stoppering the flask and shaking vigorously. To the xylene-sodium mixture was then added 100 g. of ethyl- β -(3-carbo-ethoxy-piperidino)propionate and the mixture heated in an oil-bath. When the liquid inside the flask reached a temperature of about 130° a vigorous reaction set in with the liberation of sufficient heat to cause the xylene to boil for 15–20 minutes. The temperature of the oil-bath was maintained between 140–150° for about 45 minutes after the primary reaction had ceased. This was

necessary in order to obtain maximum yields. The end of the reaction was shown by an excessive foaming of the contents of the flask. The flask was then cooled, whereupon the contents turned to a semi-solid mass. This product was then mixed with 150–200 cc. of ice water, and the xylene layer separated. The aqueous layer was extracted with 150 cc. of ether and this extract added to the xylene layer. This ether-xylene solution will be referred to later.

The aqueous solution obtained above was dark red in color. It was kept at a temperature of 0–5° and acidified with hydrochloric acid until acid to congo red. Upon acidification the color of the solution changed from a dark red to a light yellow. To the cold acid solution, potassium carbonate was added until it was distinctly alkaline, and the resulting alkaline solution was extracted with 150cc. portions of ether until test portions of the ether, when shaken with a dil. acidified aqueous solution of ferric chloride, caused no pronounced reddish purple coloration of the aqueous layer. The ether extracts (usually four) were concentrated to a volume of about 100 cc. and dry hydrogen chloride was passed in. The hydrochloride of the keto ester precipitated usually in an amorphous form.

The amorphous keto ester hydrochloride was crystallized by the following procedure. The material from the ether precipitation was dissolved in 15 cc. of warm absolute alcohol. To this solution dry ether was added until a faint cloudiness appeared, at which point the solution was cooled to about —12°. By scratching the sides of the container with a stirring rod, crystallization was started. Ethyl isogranatonine-carboxylate hydrochloride crystallized as white microscopic crystals which melted at 187–189°. It was extremely soluble in water, 95% alcohol and absolute alcohol. Only a trace of it added to a dil. ferric chloride solution gave a deep reddish-purple coloration. The yield of recrystallized material from the above run was 5.5–6.5 g. or 6–7%. From 1 to 1.5 g. of uncrystallizable material remained in the mother liquors.

Analyses. Subs., 0.1035, 0.1465: AgCl, 0.0590, 0.0850. Calc. for C₁₁H₁₈O₅NCl: Cl, 14.34. Found: 14.12, 14.34.

Internal condensations of this diester were attempted also with sodium ethylate in benzene and sodium in toluene and cymene. At the temperatures obtained with benzene and toluene the ester was left practically unchanged. Sodium in cymene, however, did completely condense the ester, but the products were of high molecular weight and it was not possible to isolate any of the cyclic keto ester by the procedure used in isolating it from the sodium-xylene condensation.

Ethyl Isogranatonine-carboxylate (VI).—A mixture of 4 g. of ethyl isogranatonine-carboxylate hydrochloride and 10 cc. of saturated potassium carbonate solution was shaken and then extracted twice with 20cc. portions of ether. The ether layer was separated and the ether then distilled. The remaining ester was placed in a small distilling system and the system evacuated to a pressure of 8 mm. The distilling flask was then immersed directly in an oil-bath at a temperature of 150–160°. The keto ester distilled at 137–139° (8 mm.); d_{20}^{20} , 1.1381; n_{1}^{18} , 1.5070; yield, 2.2 g., or 60%. It was a thick, colorless oil, insoluble in water, soluble in acid and alkali, and gave a pronounced coloration with acidified ferric chloride solution. The remainder of the ester was left in the distilling flask, probably partly as an inner salt (VII).

Analyses. Subs., 0.7185, 0.6905: 34.60, 33.40 cc. of 0.0969 N HCl. Calc. for $C_{11}H_{17}O_{1}N$: N, 6.63. Found: 6.55, 6.57.

When the crude ethyl isogranatonine-carboxylate obtained as described above by the evaporation of the ether was redissolved in ether and allowed to stand, white hygroscopic crystals separated in 12 to 24 hours. These were insoluble in ether. By acidifying with hydrochloric acid and repeating the process described above the oily isomer was again obtained.

An attempt was made to prove the presence of the isomeric ketonic ester (VIII) in the xylene-ether layer. This layer from condensations representing 400 g. of ethyl β -(3-carbo-ethoxy-piperidino)propionate was extracted with hydrochloric acid. The hydrochloric acid layer was made alkaline with potassium carbonate and extracted with ether. After evaporation of the ether 15 g. of an oil was obtained. This was refluxed with 150 cc. of 20% hydrochloric acid for 4 hours in order to hydrolyze it to the corresponding amino ketone. No product, however, was obtained.

Ethyl Isogranatoline-carboxylate Hydrochloride (IX). REDUCTION WITH SODIUM AMALGAM.—A solution of 5 g. of ethyl isogranatonine-carboxylate hydrochloride in 1 liter of 5% hydrochloric acid was placed in a 20cm. evaporating dish. Sodium amalgam (3%) was added in small pieces at a rate sufficient to maintain a vigorous evolution of gas. At the same time the temperature of the solution was kept below 20° by an external ice-bath and the reaction of the solution was kept acid to congo red by the addition of 50cc. portions of concd. hydrochloric acid when the solution appeared alkaline to the indicator. About 1500 g. of 3% sodium amalgam, added during 5 hours, was required to complete the reduction, the end of which was shown by a negative ferric chloride test. When this point was reached the mercury was separated and the aqueous layer filtered. The colorless aqueous solution was evaporated to dryness under diminished pressure and the resulting salt residue treated with two successive 300cc. portions of hot 95% alcohol. The resulting alcoholic solution, after removal of the sodium chloride, was evaporated to complete dryness under diminished pressure. The straw-colored, amorphous residue was covered with 500 cc. of 5-6% alcoholic hydrochloric acid and esterified by refluxing for 12 hours. The alcoholic hydrochloric acid was removed under diminished pressure and the residue was treated with 25 cc. of saturated potassium carbonate solution, then extracted with ether. The ether extract was concentrated to a volume of 100 cc. and dry hydrogen chloride was passed in. The hydrochloride of the base precipitated as a brown amorphous mass.

This amorphous material was crystallized as was the ethyl isogranatonine-carboxylate hydrochloride. The first crystallization yielded a light brown material which after three crystallizations appeared as practically colorless, microscopic crystals which melted at 199–201° (Isomer A); yield, 0.35 g., or 7%.

Analyses. Subs., 0.0810, 0.0800: AgCl, 0.0465, 0.0454. Calc. for $C_{11}H_{20}O_2NCl$: Cl, 14.23. Found: 14.20, 14.05.

From the mother liquors of the crystallization described it was impossible to obtain any more crystalline material, so they were combined, evaporated and the free base was liberated into ether by means of a saturated potassium carbonate solution. The ether was removed from the extract and the remaining oil subjected to distillation at 5 mm. pressure. It was dissolved in dry ether and the hydrochloride prepared and crystallized. After one crystallization the product melted at $199-201^{\circ}$. A mixed melting point with the crystals (Isomer A) obtained as described above was $170-175^{\circ}$. This product was Isomer B and the yield was 0.450 g., or 9%. There remained in the mother liquors of B 0.6 g. of uncrystallizable material.

Analyses. Subs., 0.1047, 0.1022: AgCl, 0.0589, 0.0581. Calc. for $C_{11}H_{20}O_{3}NCI$: Cl, 14.23. Found: 13.95, 14.10.

CATALYTIC REDUCTION.—A solution of 4 g. of ethyl isogranatonine-carboxylate hydrochloride in 50 cc. of absolute alcohol was shaken with hydrogen at 4 atmospheres' pressure in the presence of 2 g. of platinum oxide catalyst. Every 12 hours the catalyst was shaken with air and at 24-hour intervals 0.5 g. of fresh catalyst was added. The reduction was complete, as shown by a negative ferric chloride test, in 85 hours. The platinum was filtered off and the solution evaporated to dryness under diminished pressure.

The residue on recrystallization gave 2.5 g. (62.5%) of a product which was identical with Isomer B from the sodium amalgam reduction.

Ethyl Benzoyl-isogranatoline-carboxylate Hydrochloride (X). Benzoyl Chloride Benzoyl Chloride Benzoyl Chloride. In a 100cc. flask fitted with a ground-glass reflux condenser was placed 3 g. of ethyl isogranatoline-carboxylate hydrochloride (Isomer B) and 10 cc. of freshly distilled benzoyl chloride. The flask was then heated in an oil-bath to 140–160°. At this temperature a vigorous evolution of hydrogen chloride took place and in 20 minutes the reaction was complete. The resulting solution was cooled and diluted with 75 cc. of ether. The hydrochloride of the benzoyl derivative precipitated as a light brown, amorphous mass. The ether solution was poured off and the precipitate dissolved in 20 cc. of warm absolute alcohol. This solution was heated with 0.1 g. of bone black and filtered. From the filtrate the hydrochloride of the benzoyl derivative was obtained in pure white crystals by a method analogous to that described for ethyl isogranatonine-carboxylate hydrochloride; yield, 3.4 g., or 80%.

Analyses. Subs., 0.1044, 0.1058: AgCl, 0.0415, 0.0429. Subs., 0.4760: 13.51 cc. of 0.0951 N HCl. Subs., 0.2030: CO₂, 0.4523; H₂O, 0.1280. Calc. for $C_{18}H_{24}O_4NCl$: C, 61.07; H, 6.84; N, 3.96; Cl, 10.03. Found: C, 60.77; H, 7.00; N, 3.78; Cl, 9.84, 10.03.

An attempt was made to obtain this benzoylation product by the action of benzoic anhydride in toluene upon ethyl isogranatoline-carboxylate, obtained from the hydrochloride by the action of saturated potassium carbonate. No benzoylation product was obtained.

Summary

- 1. A method for the preparation of a derivative of a new bicyclic nucleus containing a nitrogen atom common to both rings has been developed. The new nucleus has been called isogranatanine because it is isomeric with granatanine.
- 2. The particular derivative especially investigated was ethyl benzoylisogranatoline-carboxylate, prepared by reduction of the ethyl isogranatonine-carboxylate and subsequent benzoylation.
- 3. The ethyl benzoyl-isogranatoline-carboxylate hydrochloride is isomeric with homococaine hydrochloride, and is a local anesthetic. It is considerably more toxic and less anesthetic than cocaine. Its 2% solution is irritating to a rabbit's cornea and does not cause dilation.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY, UNIVERSITY OF WISCONSIN]

ARSENATED N-ARYLAMINO ALCOHOLS1

By Cliff S. Hamilton Received August 9, 1923

The action of ethylene chlorohydrin on aromatic amines was first studied by Knorr.² He found that when equivalent amounts of aniline and ethylene chlorohydrin were heated together in a closed tube at 110° for one hour, 2-anilino-ethanol was the chief product. More recently Rindfusz and Harnack³ have shown that N-arylamino alcohols can be prepared by boiling aniline with ethylene chlorohydrin or with trimethylene chlorohydrin in the presence of sodium carbonate.

This investigation was undertaken in order to study the action of chlorohydrins on aromatic arsonic acids, containing an amino group in the ring. The condensation took place in the case of p-arsanilic acid. With m-arsanilic acid, 3-amino-4-methyl-phenylarsonic acid and 3-amino-4-hydroxy-phenylarsonic acid,—that is, compounds containing the amino group in the meta position with respect to the arsenic,—negative results were obtained.

The arsonated N-arylamino alcohols were prepared by heating the amino-aryl arsonic acid, dissolved in sodium hydroxide solution, with an excess of the chlorohydrin. They are beautiful crystalline compounds and have definite melting points. By dissolving the arsonic acids in the calculated amount of 2N sodium hydroxide solution and filtering into alcohol, sodium salts were obtained as colorless crystalline compounds, containing various amounts of water of hydration, depending upon the concentration of the alcohol used. Treatment of the arsonated N-arylamino alcohols with sodium hydrosulfite gave the yellow, highly insoluble arseno compounds.

Pharmacological experiments have been carried out with the monosodium salt of 2-p-arsono-anilino-ethanol and 3-p-arsono-anilino-propanol. As was expected, the latter, having the longer side chain, was the more toxic. From preliminary experiments, 3-p-arsono-anilino-propanol appears to have the higher trypanocidal action.

Experimental Part

Preparation of Arsono Compounds

One molecular equivalent of the amino-aryl arsonic acid was dissolved in the calculated amount of N sodium hydroxide solution to form a mono-sodium salt; 1.5 molecular equivalents of the chlorohydrin was then added

- ¹ This work was made possible by a grant from the Public Health Institute, Chicago. Some of the products are being studied pharmacologically in this Laboratory under the direction of Dr. A. S. Loevenhart.
 - ² Knorr, Ber., 22, 2092 (1889).
 - ³ Rindfusz and Harnack, This Journal, 42, 1720 (1920).

and the mixture boiled under a reflux condenser for 4 to 5 hours. The solution deposited almost colorless crystals on cooling. Concd. hydrochloric acid was added to the cold mixture to hold any unchanged p-arsanilic acid in solution and the product was filtered off and washed carefully with water. It was purified by recrystallization from hot water.

2-p-Arsono-anilino-ethanol, CH₂OHCH₂NHC₆H₄AsO₈H₂.—This compound prepared from p-arsanilic acid and ethylene chlorohydrin was obtained in 35-40% yields. The colorless needles, which melt at 167-168° (uncorr.), are soluble in hot water and dil. alkalies, but are insoluble in ether and benzene.

Analyses. Subs., 0.1989, 0.1994: 32.40, 32.60 cc. of 0.0464 N iodine soln. Subs., 0.4011, 0.4005: 14.95, 15.05 cc. of 0.1 N HCl soln. Calc. for $C_8H_{12}O_4NAs$: N, 5.36; As, 28.73. Found: N, 5.22, 5.26; As, 28.37, 28.47.

Monosodium Salt.—Ten g. of 2-p-arsono-anilino-ethanol was dissolved in 19 cc. of 2 N sodium hydroxide solution and the solution was filtered in a fine stream into 95% alcohol. Colorless crystals were deposited immediately. The yield was almost quantitative.

Analyses. Sample dried at 105°. Subs., 0.1992, 0.1998: 30.20, 30.35 cc. of 0.0464 N iodine soln. Subs., 0.4001, 0.3992: 14.50, 14.20 cc. of 0.1 N HCl. Calc. for $C_8H_{11}O_4$ -NAsNa; N, 4.94; As, 26.50. Found: N, 5.07, 4.98; As, 26.41, 26.46.

Mono-ammonium Salt.—Using ammonium hydroxide in place of sodium hydroxide solution, this compound was prepared by the method outlined under the sodium salt, as colorless needles, readily soluble in cold water.

Analyses. Sample dried at 105°. Subs., 0.1991, 0.2003: 32.40, 32.70 cc. of 0.0436 N iodine soln. Subs., 0.3012, 0.2996: 21.42, 21.38 cc. of 0.1 N HCl. Calc. for C_8H_{14} - O_4N_2As : N, 10.07; As, 26.97. Found: N, 9.96, 9.99; As, 26.65, 26.74.

Barium Salt.—This compound was prepared by dissolving the arsonic acid in hot water and adding the calculated amount of a barium hydroxide solution. A white precipitate formed on standing that was insoluble in alcohol, but somewhat soluble in water.

Analyses. Sample dried at 105°. Subs., 0.2002, 0.1999: 27.10, 27.50 cc. of 0.0436 N iodine soln. Calc. for $C_{16}H_{22}O_{8}N_{2}As_{2}Ba$: As, 22.88. Found: 22.17, 22.53.

3-p-Arsono-anilino-propanol, CH₂OH(CH₂)₂NHC₅H₄HsO₅H₂.—Following the general procedure for the preparation of arsono compounds, 21.7 g. of p-arsanilic acid when treated with 14 g. of trimethylene chlorohydrin, gave 8 g. of product. Recrystallization from hot water gave colorless crystals; m. p., 160–161° (uncorr.).

Analyses. Subs., 0.2016, 0.2004: 32.50, 32.40 cc. of 0.0452 N iodine soln. Subs., 0.4052, 0.4041: 14.30, 14.42 cc. of 0.1 N HCl. Calc. for C₂H₁₄O₄NAs: N, 5.09; As, 27.27. Found: N, 4.94, 4.99; As, 27.42, 27.40.

SODIUM SALT.—Four g. of the corresponding arsonic acid gave 3.9 g. of the sodium salt as colorless crystals from 95% alcohol, on standing.

Analyses. Subs. (dried in oven at 105°), 0.1987, 0.1991: 30.60, 30.60 cc. of 0.0443 N iodine soln. Subs., 0.3991, 0.3980: 13.61, 13.52 cc. of 0.1 N HCl. Calc. for C₂H₁₈-O₄NAsNa: As, 25.25; N, 4.71. Found: N, 4.77, 4.75; As, 25.60, 25.55.

AMMONIUM SALT.—By dissolving the arsonic acid in ammonium hydroxide and filtering the solution into alcohol, colorless needles were obtained in good yields.

Analyses. Subs. (dried in oven at 105°), 0.1898, 0.1901: 30.00, 29.90 cc. of 0.0436 N iodine soln. Subs., 0.3008, 0.3006: 20.48, 20.51 cc. of 0.1 N HCl. Calc. for C₉H₁₆O₄-N₂As: N, 958; As, 25.68. Found: N, 9.54, 9.55; As, 25.89, 25.76.

BARIUM SALT.—A white powder, prepared as was the barium salt of 2-p-arsono-anilino-ethanol, was obtained.

Analyses. Subs. (dried in oven at 105°), 0.2017, 0.2003: 26.40, 26.20 cc. of 0.0436 N iodine soln. Calc. for $C_{17}H_{24}O_8N_2A_{52}Ba$: As, 21.89. Found: 21.43, 21.42.

Preparation of Arseno Compounds⁴

One molecular equivalent of the arsonated N-arylamino alcohol was dissolved in hot water. This solution was added with shaking to a solution of 10 equivalents of sodium hydrosulfite in 550 equivalents of water, after the latter solution had been previously treated successively with 6 equivalents of 10 N sodium hydroxide solution and 10 equivalents of crystalline magnesium chloride and filtered from the magnesium hydroxide formed. After this mixture had been heated on a water-bath and frequently shaken for $^{1}/_{2}$ hour, the yellow precipitate which formed was filtered off, washed with water, alcohol, and ether and dried in a vacuum.

2-p-Arseno-anilino-ethanol, CH₂OHCH₂NHC₆H₄As=AsC₆H₄NHCH₂CH₂OH.— Five g. of 2-p-arsono-anilino-ethanol upon reduction, as outlined above, gave a 30% yield of the yellow arseno compound. It is insoluble in common organic solvents and does not melt below 250°.

Analyses. Subs., 0.1779, 0.1783: 38.70, 38.60 cc. of 0.0440 N iodine soln. Calc. for $C_{16}H_{20}O_2N_2As_2$: As, 35.57. Found: 35.93, 35.77.

3-p-Arseno-anilino-propanol, CH₂OH(CH₂)₂NHC₆H₄As=AsC₅H₄NH(CH₂)₂CH₂-OH.—The reduction of 10 g. of 3-p-arsono-anilino-ethanol gave 4.5 g. of the arseno product. It does not melt below 250° and has the usual properties of arseno derivatives. Analyses. Subs., 0.1984, 0.1990: 39.80, 39.90 cc. of 0.0440 N iodine soln. Calc. for C₁₅H₂₄O₂N₂As₂: As, 33.33. Found: 33.14, 33.12.

Arsonated s-Di-anilino Ethane

s-Bis(p-arsono-anilino) ethane, $H_2O_2AsC_6H_4NH(CH_2)_2NHC_6H_4AsO_2H_2$.—To a solution of 21.7 g. of p-arsanilic acid in 100 cc. of N sodium hydroxide solution was added 12 g. of ethylene dibromide and the mixture was boiled under a reflux condenser. The ethylene dibromide gradually dissolved, and a white solid began to form. After the mixture had been boiled for two hours, it was cooled, 10 cc. of concd. hydrochloric acid was added to hold the unchanged arsanilic acid in solution, and the product was separated by filtration. It was purified by dissolving it in 10% sodium hydroxide solution, filtering and acidifying the filtrate with concd. hydrochloric acid; yield, 7 g.

The product is readily soluble in dil. alkalies, two molecular equivalents of sodium hydroxide being required for the neutral salt. It does not melt below 250°.

Analyses. Subs., 0.1888, 0.1992: 33.10, 34.80 cc. of $0.0494\ N$ iodine soln. Subs., 0.3871, 0.3992; 16.65, 17.05 cc. of 0.1 N HCl. Calc. for $C_{14}H_{18}O_{5}N_{2}As_{2}$: N, 6.08; As, 32.60. Found: N, 6.02, 5.98; As, 32.52, 32.41.

Monosodium Salt: Five g. of the above arsonic acid was dissolved in the calculated amount of 2 N sodium hydroxide solution to form the neutral salt, and the solution was filtered in a fine stream into 95% alcohol; 3.8 g. of colorless crystals was deposited.

Analyses. Subs. (dried in oven at 105°), 0.2009, 0.2016: 33.40, 33.45 cc. of 0.0474 N iodine soln. Calc. for $C_{14}H_{16}O_{6}N_{2}As_{2}Na_{2}$: As, 29.76. Found: 29.59, 29.53.

⁴ Meister, Lucius and Bruning, Ger. pat. 206,057.

Summary

- 1. The action of chlorohydrins on amino-aryl arsonic acids has been investigated, and the properties of the resulting compounds and some of their derivatives have been described.
- 2. The condensation of ethylene dibromide with p-arsanilic acid has been studied, and the neutral sodium salt prepared.

Madison, Wisconsin

[Contribution from the Department of Chemical Hygiene, Johns Hopkins University]

ANALYSIS OF THE JERUSALEM ARTICHOKE¹

By A. T. SHOHL

RECEIVED AUGUST 23, 1923

The Jerusalem artichoke, helianthus tuberosus, has long been known and used as an article of food. The common books on food analysis and food values do not, however, list it.

There is an analysis by Strauss² and one by Langworthy³ to which the reader is referred for a further description of the occurrence, habits and methods of preparing the Jerusalem artichoke for table use.

This investigation was undertaken with the idea of establishing the importance of the Jerusalem artichoke in the treatment of diabetics, but suitable clinical material has not been available. The following analysis is published in the hope of suggesting such use to others.

It is well known that this tuber contains large amounts of inulin, a carbohydrate which on hydrolysis yields levulose. Inulin in the form of "Topinambur" (Jerusalem artichoke) was used in the treatment of diabetes as early as 1851 by Bouchardat.⁴ Külz⁴ in 1874 showed that inulin was burned in the body, since diabetics excreted none in the feces. Inulin has fallen into disuse since Sandmeyer,⁴ 1894, showed that dogs with partial removal of the pancreas could not utilize inulin and Mendel,⁴ 1908, objected to its use because there are no enzymes in the body to split it. Inulin is, however, hydrolyzed by dil. acids. That there is enough acid in the gastric juice to split it has been shown by Chittenden,⁵ Lewis⁶ and Okey.⁷

Strauss8 has reopened the question and found that inulin was well

- ¹ Read at the Rochester meeting of the American Chemical Society, 1921.
- ² Strauss, Ther. Gegen., 52, 347 (1911).
- ³ Langworthy, U. S. Dept. Agr. Bull., 468 (1917).
- 4 Cited by Goudberg, Ref. 9.
- E Chittenden, Am. J. Physiol., 2, xvii (1898).
- ⁶ Lewis, J. Am. Med. Assoc., 58, 1176 (1912).
- 7 Okey, J. Biol. Chem., 39, 149 (1919).
- * Strauss, Berl. klin. Wochschr., 49, 1213 (1912).

utilized in severe cases of diabetes with acidosis. Goudberg⁹ examined the feces of the same cases and found no inulin. He also made metabolism studies with inulin and found increased production of carbon dioxide. The problem of the use in diabetes of 15 or 20 g. of inulin as Jerusalem artichoke is quite different from that in metabolism studies of 150 or 200 g. of pure inulin. The utilization of small amounts would make a great difference in diabetes, but very little in general nutrition. Even if the Jerusalem artichoke were inert, it would still be useful in making palatable diets of suitable bulk for diabetics on greatly restricted food intake. If suitable clinical studies confirm the work of Strauss as does our limited experience and that of Joslin and Root, 10 that there is no increased sugar elimination in diabetes; and if at the same time metabolism experiments show increased utilization of carbohydrate as demonstrated by Goudberg, Jerusalem artichoke should become a valuable adjunct in the dietetic treatment of diabetes.

Analysis

Inulin was prepared from tubers obtained in December and January, when storage is most abundant. Plimmer's method¹¹ was used. The material was a white powder, soluble in hot water and precipitated by 50% alcohol. Fehling's test gave no reduction before inversion, but positive reduction after inversion. After inversion levorotation was increased.

The juice of the artichoke was expressed and its Sörensen value (PH) by the colorimetric method of Clark¹² was found to be 5.0. The antineuritic properties have been tested in this Laboratory by Miss M. Koch and the material was found to contain water-soluble B in scant amounts.

The tubers were pared before analysis and the "edible portion" was 69% of the weight as purchased. The analysis was performed according to the methods of the Official Agricultural Chemists and the results given in Table I have been compared with those given by Strauss⁸ and Langworthy. The agreement is close.

Table I
Percentage Composition of the Edible Portion of Jerusalem Artichoke

%	Moisture	N × 6.25 Protein	True protein	Fat	Carbo- hydrate	Fiber	Ash
Strauss	72.62	1.97	0.81		13.08		1.89
Langworthy	78.7	2.5	•;•	0.2	17.5	0.8	1.1
Shohl	79.0	3.1	0.9	0.2	15.5	0.8	1.1

The carbohydrate was determined by extracting either the fresh vegetable or the air-dried material for 72 hours with boiling water. The extract

⁹ Goudberg, Z. exptl. Path. Therap., 13, 310 (1913).

¹⁰ Joslin and Root, J. Am. Med. Assoc., 80, 1727 (1923).

¹¹ Plimmer, "Practical Organic and Biochemistry," London, 1915, p. 213.

¹² Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., 1921.

was hydrolyzed by refluxing for 2 hours with 10% of hydrochloric acid. The levulose was determined by Benedict's method. Fifty mg. of dextrose is equivalent to 52 mg. of levulose. The carbohydrate content was found to be 15.5%.

The nitrogen determination of the extract made as described above shows that of the nitrogen listed as "protein" 71.5% is readily water-soluble and hence not protein. The amino acid nitrogen determined by Van Slyke's method¹⁴ is 27.5% of the water-soluble nitrogen.

Summary

Analysis of the Jerusalem artichoke shows that it contains 15.5% of inulin. Of the total nitrogen, 71.5% is water-soluble. It contains but small amounts of water-soluble B vitamin. Its use in the treatment of diabetes should be reinvestigated. Analysis, clinical experience and a single experiment in metabolism indicate that the Jerusalem artichoke is a valuable adjunct in the dietetic treatment of diabetes.

BALTIMORE. MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, No. I, 31]

REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION. IV. ACTION OF THE ALKALI METALS ON TRIPHENYLMETHYL AND ITS COMPOUNDS

By Charles A. Kraus and T. Kawamura Received September 6, 1923

The triphenylmethyl group is the first example discovered of a class of compounds exhibiting certain characteristic properties. What attracted particular notice in the first instance was the fact that these compounds appeared to form an exception to the quadrivalence of the carbon atom. These groups, however, possess many other properties which serve to distinguish them, as well as their compounds, from other organic compounds. Thus, compounds of the triphenylmethyl group with the halogens exhibit electrolytic properties in solutions in certain solvents, while the groups also yield compounds with strongly electropositive metals, such as sodium, the properties of which characterize them as exceptional. We now know that many other elements yield compounds resembling the triphenylmethyl group as, for example, lead, tin, mercury and nitrogen, although the properties of these groups have not been extensively investigated.

- 13 Benedict, J. Am. Med. Assoc., 57, 1193 (1911).
- 14 Van Slyke, J. Biol. Chem., 12, 275 (1912).
- ¹ Rügheimer, Ann., 364, 53 (1909).
- ² E. Krause, Ber., 54, 2060 (1921); 55, 888 (1922).
- ² Kraus, This Journal, 35, 1732 (1913).
- 4 H. Weiland, Ber., 48, 1078, 1098, 1112 (1915).

Some years ago one of the present authors⁵ made the observation that the triphenylmethyl halides, when treated with alkali metals in liquid ammonia solution, yield a compound highly soluble in liquid ammonia, exhibiting a strong red color by transmitted light and a greenish-violet color by reflected light in concentrated solution. In view of the strongly electropositive nature of sodium and the electronegative nature of chlorine, it appeared probable that a reaction occurred in which sodium chloride was formed, leaving behind either the free group or a compound between this group and sodium. This reaction has accordingly been studied further.

Experimental Part

Action of Sodium on Triphenylmethyl Chloride.—The reactions were carried out in an apparatus similar to that which has already been described in an earlier number of this series.⁶

As stated, metallic sodium reacts with the triphenylmethyl halides in liquid ammonia solution. Because of the low solubility of the halides, reaction takes place somewhat slowly; this difficulty may, however, be overcome by stirring the reaction mixture by means of a stream of ammonia vapor passed through the solution. The compound formed is very soluble. Under favorable conditions it may be obtained in the form of reddish needles. No gas is evolved in the reaction with triphenylmethyl chloride.

Five g. of triphenylmethyl chloride was treated with 0.825 g. of metallic sodium in liquid ammonia. At the end of the reaction about 50 cc. of pure toluene was added, after which the bath of ammonia surrounding the reaction chamber was removed. The compound is soluble in toluene and separation was effected from the sodium chloride by filtering through a Gooch crucible in an apparatus in which the air was displaced by means of ammonia vapor. The residue on the filter consisted of sodium chloride with a small amount of sodium hydroxide, due presumably to the presence of a slight amount of moisture. The sodium chloride obtained weighed 0.98 g., corresponding approximately to one-half the sodium originally introduced.

It follows that one molecule of triphenylchloromethane reacts with two atoms of sodium to form one molecule each of sodium chloride and a compound of sodium with the triphenylmethyl group. Reaction takes place according to the equation

$$(C_6H_5)_3CC1 + 2Na = (C_6H_5)_3CNa + NaC1$$
 (1)

The compound formed between sodium and the triphenylmethyl group is very reactive, even at the temperatures of liquid ammonia. With water

- ⁵ Kraus, unpublished observations.
- ⁶ White, This Journal, 45, 779 (1923).
- ⁷ This same compound had previously been described by Schlenk and Ochs [Ber., 49, 608 (1916)], although this publication was not available when the present investigation was carried out. It may be noted that, as here prepared, the sodium triphenylmethyl compound contains one molecule of ammonia, as has since been shown by Dr. R. Rosen in this Laboratory.

it reacts to form sodium hydroxide and triphenylmethane, as was shown by characterizing the products of the reaction. Thus

$$(C_6H_5)_3CNa + H_2O = (C_6H_5)_3CH + NaOH.$$
 (2)

The compound combines readily with oxygen to form a white product, the nature of which was not determined at the time.8

With ammonium chloride in liquid ammonia, sodium triphenylmethyl yields an immediate pinkish precipitate and the red color disappears. This compound, however, is unstable, since it turns white slowly on standing at the temperature of boiling ammonia. Apparently the initial reaction consists in a replacement of the sodium by the ammonium group to form an ammonium triphenylmethyl, which subsequently decomposes according to the equation

$$(C_6H_5)_3CNH_4 = (C_6H_5)_3CH + NH_3.$$
 (3)

Triphenylmethane was characterized as an end-product in this reaction. Sodium triphenylmethyl reacts with bromobenzene and triphenylchloromethane to form tetraphenylmethane and triphenylmethyl, respectively, as will be described below. Sodium triphenylmethyl is moderately soluble in toluene and benzene, but is insoluble in petroleum ether and ligroin.

Action of Metallic Sodium on Triphenylmethane.—The nature of the compound formed between sodium and the triphenylmethyl group was further elucidated by the action of sodium on triphenylmethane in liquid ammonia solution. When triphenylmethane is treated with metallic sodium in equivalent amount in liquid ammonia, reaction takes place somewhat slowly with the formation of sodium triphenylmethyl and the evolution of hydrogen. The compound formed, as was shown by its properties at the end of the reaction, is the same as that formed by the action of sodium on triphenylmethyl chloride. This method of preparing sodium triphenylmethyl has the advantage that the solutions of the compound in ammonia may be obtained without the presence of sodium chloride. Three g. of triphenylmethane reacted completely with 0.2829 g. of sodium in the course of about an hour. Reaction takes place according to the equation

$$(C_6H_5)_3CH + Na = (C_6H_5)_3CNa + \frac{1}{2}H_2.$$
 (4)

What is perhaps most striking in the case of this reaction is the fact that hydrogen attached to a saturated carbon atom is replaced by sodium. Evidently, triphenylmethane is to be looked upon as a very weak monobasic acid. Further evidence to this effect will be adduced in a subsequent article.

Synthesis of Triphenylmethyl in Liquid Ammonia.—If sodium triphenylmethyl is present in liquid ammonia solution, we should expect it to be a comparatively weak electrolyte because of the weakly electronegative

⁸ This reaction has subsequently been studied by Dr. R. Rosen in this Laboratory. The results will appear later.

properties of the triphenylmethyl group. If, therefore, we were to treat sodium triphenylmethyl with triphenylmethyl chloride, we should expect the following reaction to take place

$$(C_6H_5)_3CNa + (C_6H_5)_3CCI = 2(C_6H_5)_3C + NaCI$$
 (5)

The sodium compound was prepared from equivalent amounts of sodium and triphenylchloromethane in liquid ammonia according to the method previously described. An equivalent amount of triphenylchloromethane was then added to the solution. In liquid ammonia, the reaction between triphenylchloromethane and sodium triphenylmethyl takes place only very slowly because of the low solubility of the former substance. When toluene is added to the mixture, both compounds are dissolved and reaction takes place immediately. The red color due to the sodium compound disappears, while the yellow color which is characteristic of triphenylmethyl makes its appearance. By stirring the solution with a stream of ammonia vapor the rate of the reaction is greatly accelerated.

Dry air was passed through this solution, whereby the free group was oxidized, the yellow color disappearing and a white amorphous precipitate being formed. The contents of the tube were transferred to a small distilling flask and the toluene was distilled. Organic impurities were removed by extraction with ether, in which the peroxide, formed as a result of the process of oxidation, is insoluble. The residue was washed with water to remove sodium chloride, and the resulting compound, which remained behind on the filter paper, was recrystallized from hot benzene. The melting point was found to be 186° sharp, which corresponds to that of the peroxide of triphenylmethyl. Triphenylmethyl is evidently formed according to Equation 5.

Triphenylmethyl in liquid ammonia reacts at once with metallic sodium to form sodium triphenylmethyl, whose presence is made evident by its characteristic red color. The compound was further characterized by the formation of triphenylmethane when water was added to the solution, according to Equation 2.

No reaction appears to take place between ammonium chloride and the free triphenylmethyl group.

Sodium triphenylmethyl appears to be entirely stable in liquid ammonia solution and in the presence of ammonia vapor at low temperatures. At higher temperatures, however, the solid decomposes. Previous investigators have noted that sodium triphenylmethane is acted upon by ammonia vapor with the formation of sodium amide and triphenylmethane.⁹ This reaction has since been studied more in detail and will be described in another paper.

Synthesis of Tetraphenylmethane.—Tetraphenylmethane may be readily synthesized through the action of bromobenzene on sodium triphenylmethyl. When the phenyl bromide is added directly to the solution of the sodium compound in liquid ammonia, reaction takes place slowly. The reaction is hastened if toluene is added to the liquid ammonia solution of triphenylmethyl. For this purpose the major portion of the ammonia is evaporated. The compound precipitated in this process must not be allowed to warm much above the boiling point of ammonia, as otherwise it is decomposed. When the excess ammonia has been evolved, phenyl bromide is added and the contents of the tube are allowed to warm slowly

⁹ Schlenk and Ochs, Ref. 7.

to room temperature. Tetraphenylmethane is formed according to the reaction

$$(C_6H_5)_3CNa + (C_6H_5)Br = (C_6H_5)_4C + NaBr$$
 (6)

Ten g. of triphenylchloromethane was treated with 1.65 g. of metallic sodium, the ammonia evaporated and toluene added as described; 55 cc. of pure dry bromobenzene was then added. The mixture was stirred by passing a stream of ammonia gas through the reaction tube at the temperature of liquid ammonia. At the end of about half an hour the bath of boiling ammonia was removed and the contents of the tube allowed to warm slowly to room temperature, after which the tube was placed in a water-bath and the contents brought to a temperature of 100°. As the temperature rises, the excess phenyl bromide dissolves the solid present, yielding a solution which is dark yellow in color. The insoluble residue consists chiefly of sodium bromide. On completion of the reaction, the contents of the tube were transferred to a small distilling flask and the excess of bromobenzene was evaporated. The residue of solid in the distilling flask was treated with ether and the mixture filtered. Any triphenylchloromethane which had not been acted upon was thus carried off with the ether. The residue on the filter consisted of tetraphenylmethane and sodium bromide, the latter being then removed with water. The residue was dried and recrystallized from hot benzene by slow cooling. From acetic anhydride the compound may be obtained in the form of long, silky needles; yield 4.35 g., or 37.8%. Tetraphenylmethane is practically insoluble in alcohol and ether, petroleum ether, ligroin, cold acetic acid and cold acetic anhydride; and is soluble in hot acetic acid, acetic anhydride, benzene, toluene and ethylene bromide. Recrystallization from hot acetic acid is recommended for the purpose of obtaining large crystals.

The molecular weight of the compound was determined in benzene by the boiling-point method. Three determinations gave 310.3, 315.4, 317.5, which is in good agreement with the calculated value of 320.

Action of Potassium on Triphenylchloromethane.—The action of potassium on triphenylchloromethane is similar to that of sodium, two equivalents of potassium being required to complete the reaction. Potassium triphenylmethyl has the same appearance as sodium triphenylmethyl and exhibits very similar properties. It exhibits, however, this marked difference, namely, that while sodium triphenylmethyl is unstable in the presence of ammonia, potassium triphenylmethyl is stable even at a temperature of 100°. Another marked difference is that it has not been found possible to synthesize the riphenylmethyl group by the action of triphenylmethyl chloride on potassium triphenylmethyl, as will be shown below.

Action of Potassium Triphenylmethyl on Triphenylchloromethane.— The attempt was made to synthesize triphenylmethyl by the same procedure which was employed in the case of sodium triphenylmethyl. In no case, however, was any evidence of the formation of the free triphenylmethyl group obtained.

Reaction was found to take place on adding triphenylchloromethane to potassium triphenylmethyl in the presence of toluene, and was completed in the course of a few minutes, the red color of the potassium compound disappearing and a yellow color taking its place, while a small amount of solid impurity was left in the bottom of the reaction

tube. The ammonia was evaporated, the residue heated to 70° and the toluene distilled under reduced pressure. The residue left in the reaction tube was treated with ligroin and then filtered. From the filtrate fine white crystals were obtained, m. p. 210° , and from the residue on the filter paper a powder was obtained, m. p. $235-236^{\circ}$. This experiment was repeated a number of times with practically the same results, the chief product of the reaction being the compound melting at 210° . From 50 to 60° % of the original compound was obtained in this form.

Tests were made for the presence of free triphenylmethyl in the toluene solution, by passing air through this solution. No trace of peroxide could be obtained, the chief product again being a compound melting at 210°. The melting point of this compound agrees with that of the so-called stable hexaphenylethane obtained by Anschütz. 10 That this compound is actually hexaphenylethane may be doubted.

Action of Calcium on Triphenylchloromethane.—Metallic calcium reacts readily with triphenylchloromethane in ammonia solution to form a reddish-brown compound. From its appearance it may be inferred that the reaction is similar to that which takes place in the case of sodium. The compound is much less stable than the corresponding sodium compound, since it decomposes almost at once at ordinary temperatures and slowly even at liquid ammonia temperatures. A white product results, the nature of which was not further studied.

Mechanism of the Reduction Process

The action of sodium on triphenylmethyl and its compounds is of interest, not only because of the light it throws on the nature of the triphenylmethyl group, but also because of the insight it yields into the mechanism of the reduction of organic compounds by means of electropositive metals. In the metal solutions, the active reducing agent is the free negative electron, and the process of reduction consists in the combination of the negative electron with the negative constituent of the carbon compound to form a negative ion. The carbon group, on the other hand, may be left in the free condition, may combine with the negative electron to form an anion, or may react with other substances present to form various compounds. In general, in the presence of excess of the free metal, that is, in the presence of excess negative electrons, the organic group will either form a stable negative ion or react with other substances, more particularly the solvent. The initial stage of the reaction, in any case, will take place as follows: $RX + 2e^{-} = Re^{-} + Xe^{-}$. Depending upon the strength of the acid RH and the strength of the base MNH2, where M is the metallic element present in the solution, reaction may take place according to the equation, Re- + H+ = RH. In other words, if the hydrocarbon RH is a sufficiently weak acid and the base MNH2 a sufficiently weak base, the salt RM will hydrolyze according to the equation, RM + NH₃ = RH + MNH₂.

In the case of triphenylmethyl chloride, the ionic reaction may be ¹⁰ Anschütz, Ann., 395, 196 (1908).

written thus: $(C_6H_5)_8CC1 + 2e^- = (C_6H_5)_8C^- + C1^-$. Since sodium triphenylmethyl is an electrolyte in ammonia, the ionic equation above properly describes the reaction.

Solutions of triphenylmethyl chloride in liquid ammonia conduct the electric current, as do also solutions of sodium triphenylmethyl. The triphenylmethyl group is an example of a numerous class of substances the members of which exhibit amphoteric properties with respect to the positive and negative charges, that is, which are capable of existing either as anions or as cations, depending upon conditions. As has elsewhere been pointed out by one of the present authors, this is a property common to practically all the free groups. In this respect the free groups closely resemble the elements with which they are allied, namely elements which are weakly electropositive and electronegative. All such elements exhibit amphoteric properties, acting either as anions or cations, depending upon conditions, and the same is true of the free groups. The chief distinction between the groups and the elements lies in the fact that, with the exception of hydrogen, all the intermediate elements in the potential series are multivalent, while the free groups are, as a rule, univalent.

The closest analog to the free groups among the elements is hydrogen, which exhibits marked amphoteric properties, being electropositive when combined with more strongly electronegative elements as, for example, the halogens, and being electronegative when combined with the more electropositive elements as, for example, the alkali metals.

Summary

The strongly electropositive metals react with triphenylmethyl chloride in liquid ammonia to form the chloride of the metal and a compound of the metal with the triphenylmethyl group. The sodium and potassium compounds are readily soluble in liquid ammonia and are fairly soluble in benzene and toluene. The solutions exhibit a strong red color and the sodium compound has been obtained in the form of red needles. The potassium compound is stable up to 100°, the sodium compound is unstable at room temperatures, while the calcium compound is unstable even at the temperature of boiling ammonia.

The free triphenylmethyl group may be synthesized by the action of triphenylmethyl chloride on sodium triphenylmethyl in the presence of toluene. A corresponding synthesis could not be carried out with potassium triphenylmethyl. The free triphenylmethyl group in liquid ammonia reacts readily with sodium to form the sodium salt.

Tetraphenylmethane is formed by the action of phenyl bromide on sodium triphenylmethyl in liquid ammonia.

¹¹ R. Rosen, Dissertation, Clark University, 1923. ¹² Kraus, Rec. trav. chim., 42, 588 (1923).

The mechanism of the reduction of organic halides by means of the alkali metals in liquid ammonia solution is discussed.

Worcester, Massachusetts

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADDITION OF MERCURIC SALTS TO ALPHA-BETA-UNSATURATED KETONES

By Edmund B. Middleton¹ Received September 21, 1923

It is well known that mercuric salts react more or less readily with various unsaturated compounds to give products whose compositions are represented by unsaturated compound plus —HgX and —OH, if the reactionis carried out in aqueous solution, or unsaturated compound plus —HgX and —OR if the reaction is carried out in alcohol. There has been some question as to their structure, whether they are saturated compounds formed by addition to the double linkage or complex compounds of the double salt or molecular type.² For example, when ethylene is passed into a methyl alcoholic solution of mercuric acetate, it forms a compound whose composition is represented by C₂H₄. HgOCOCH₃. OCH₃ and which according to these two views, is either a molecular compound, or the saturated compound, ³ CH₂—CH₂ . The principal reason why

OCH3 HgOCOCH3

substances of this type have been regarded as molecular compounds is the ease with which the unsaturated compounds are regenerated by acids. C_2H_4 . HgX. $OCH_3 + HX \longrightarrow C_2H_4 + CH_3OH + HgX_2$. The most recent work of Adams, Roman and Sperry¹ shows conclusively that in some cases these are saturated compounds formed by addition to the double bond. The following investigation of the reaction between mercuric acetate and α,β -unsaturated ketones was undertaken with the purpose of getting further evidence on this point and on the mode of addition. The results show that α,β -unsaturated ketones with one double linkage, such as benzalacetophenone, will react with but one mol. of mercuric acetate while with dibenzalacetone, which has two double linkages, two mols. of mercuric acetate reacted. It appears from this that addition to the double linkages has taken place. Furthermore, all the compounds were white. Cinnamalacetophenone, a ketone which has two double

- ¹ National Research Fellow in Chemistry.
- ² For an account of the arguments in favor of and against 'molecular' structures, see Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., 1921, Chap. 5.
 - ³ Schoeller and Schrauth, Ber., 46, 2867 (1913). Manchot, Ber., 53, 986 (1920).
- ⁴ Adams, Roman and Sperry, This Journal, **44**, 1781 (1922). Mills and Adams, *ibid.*, **45**, 1842 (1923).

linkages, one of which is γ to the carbonyl, reacted with two molecules of alcoholic mercuric acetate, but the acetate compound has not been obtained in a form suitable for analysis, and when sodium chloride solution was added, insoluble amorphous precipitates of variable composition were obtained.

The simple α,β -unsaturated ketones were found to react readily with mercuric acetate in alcoholic solution. With benzalacetophenone, the products obtained analyzed for the ketone to which the groups —OR and HgOCOCH₃ had been added. The addition might have taken place in one of three ways: the groups could add 1, 4 to the conjugated system, like other metallic derivatives, to give a compound of the structure I; or they might possibly add 1, 2, according to either II or III.

Structure III may be discarded immediately because the mercury compounds obtained reacted with halogens, the halogen replacing the mercury group and α -halogen- β -alkoxy ketones were obtained. The α -bromo- β -ethoxy and α -bromo- β -methoxy addition products of benzalacetophenone have been isolated recently by Dufraisse and Gerald⁵ as intermediate products in the reaction of sodium alcoholate with α -bromobenzalacetophenone. The melting points and other properties given by these workers

$$\begin{array}{c} C_6H_5-CH=CBr-C-C_6H_5 + \dfrac{NaOR}{ROH} & C_6H_6-CH-CHBr-C-C_6H_6 \longrightarrow \\ 0 & OR & O \\ X \end{array}$$

$$C_6H_6-C=C-C-C_6H_6+NaX$$

OR
O

are identical with those of the bromine compounds obtained from the mercury derivatives of benzalacetophenone by replacing the mercury with bromine.

It now remains to distinguish between Structures I and II. In this connection, the reaction of mercuric acetate in alcohol solution with dibenzalacetone was studied. If the groups add 1, 4, we should expect to get only a monomercury compound with dibenzalacetone, C_0H_5 –

—OR and two —HgOCOCH₃ groups, and a dimercurated product could not have been obtained by 1, 4 addition alone. Furthermore, the com-

⁵ Dufraisse and Gerald, Compt. rend., 174, 1631 (1922).

pounds did not give mercuric oxide with sodium hydroxide solution as one might expect if they were —OHg— derivatives, so that mercury compounds of benzalacetophenone have Structure II, while the derivatives of dibenzalacetone are C_6H_5 —CH—CH—CH—CH—CH—C $_6H_5$. The mercury de-OR | | | | | | HgX O HgX OR

rivatives of unsaturated ketones are therefore analogous to the substances derived from the unsaturated esters.⁶

The behavior of these compounds was similar to that of mercury derivatives of other unsaturated compounds. Solutions of the acetates gave precipitates of the bromides or chlorides when treated with sodium bromide or chloride solution and they were decomposed by acids and by sodium iodide in the usual way. Also, they were found to be decomposed by Grignard reagents; ethylmagnesium bromide reacted with the bromomercuri-methoxy derivative of benzalacetophenone giving β -phenylvalerophenone. The last substance is obtained from benzalacetophenone itself and ethylmagnesium bromide.

As Dufraisse and Gerald⁵ have shown, the α -bromo- β -alkoxy- β -phenyl propiophenones lose hydrogen bromide with sodium alcoholate giving ketones of the structure, C_6H_5 —C—CH—C— C_6H_5 . These unsaturated CR

ketones reacted with alcoholic mercuric acetate but no "acetal" compound,

OR H
$$C_6H_5-C-C-C-C_6H_5, \ was \ obtained; \ the \ analyses \ indicated \ that \ the \ OR \ HgX \ O$$

product was diacetoxymercuri-dibenzoyl methane. The reaction was found to go best in dil. alcohol solution so it probably proceeds first, by the addition of —OH and —HgOCOCH₃, second, by the elimination of ROH and third, by the further addition of mercuric acetate.

Substitution in the benzene rings did not affect the reaction of the unsaturated ketones with mercuric acetate. Benzal-p-chloro-acetophenone reacted as readily as benzalacetophenone itself. But the reaction failed with benzaldesoxybenzoin. Nor were addition compounds formed with cyclopropane ketones. Dimethyl 2-phenyl-3-benzoyl-cyclopropane-dicarboxylate⁸ did not react with mercuric acetate in cold methyl alcohol solution nor did 1,2-dibenzoyl-3-phenyl-cyclopropane.⁹ Other cyclopropanes were tried without obtaining addition products.

It is interesting to compare the reactions of unsaturated ketones with

- 6 Schoeller, Schrauth and Struensee, Ber., 43, 695 (1910); 44, 1048 (1911)
- ⁷ Am. Chem. J., 38, 548 (1907).
- 8 Kohler and Conant, This Journal, 39, 1404 (1917).
- ⁹ Kohler and Jones, ibid., 41, 1249 (1919).

mercuric acetate and with mercuric halides. Since this work was completed. Vorländer and Eichwald¹⁰ have published an account of more compounds obtained from mercuric chloride and bromide, and unsaturated ketones. The double compounds, composed of one mol. of ketone and one mol. of mercuric halide, were stable towards alcohol, the solvent used: that is, there were no products obtained of the type, unsaturated ketone plus -OR plus -HgX. In hot alcohol they were completely dissociated into their components, mercuric halide and unsaturated ketone. The writer has found by measuring the elevation of the boiling point of acetone, that they are completely dissociated in this solvent, while the compounds described in this paper, while not entirely undecomposed, are not dissociated to this extent. The compounds obtained with mercuric halides are colored and with an unsaturated ketone with two double linkages: dianisalacetone, the product obtained by Vorländer and Eichwald, contained only one mol. of mercuric halide to one of ketone. In view of the facts known, it seems probable that the following equilibrium exists when alcoholic solutions of mercuric salts and of an unsaturated ketone such as benzalacetophenone are brought together.

When a mercuric salt such as the acetate, which is alcoholized to a relatively large extent, is used, the reaction finally goes to IV. But when HgX_2 is one of the mercuric halides, the compounds first formed are not affected by the alcohol and the equilibrium represented by Steps I, II and III may be present. In solution such an equilibrium may exist, but the compounds which finally precipitate when mercuric acetate is used are the result of the addition of —OR and $HgOCOCH_3$ to the double linkage.

Experimental Part

 α -Acetoxymercuri- β -methoxy- β -phenylpropiophenone.—A solution of 25 g. of benzalacetophenone and 38 g. of mercuric acetate in 250 cc. of absolute methyl alcohol was allowed to stand until a sample no longer gave a precipitate of mercuric oxide with sodium hydroxide sofution. The solution was concentrated by evaporation and the mercury compound crystallized; weight, 53 g. After recrystallization from methyl alcohol it melted at 115°.

Analyses. Calc. for C₁₈H₁₈O₄Hg: C, 43.31; H, 3.63; Hg, 40.2. Found: C, 43.13; H, 3.54; Hg, 40.2, 40.0.

¹⁰ Vorländer and Eichwald, Ber., 56B, 1153 (1923).

 α -Acetoxymercuri- β -ethoxy- β -phenylpropiophenone.—In a similar manner, benzalacetophenone reacted with mercuric acetate in absolute ethyl alcohol; 25 g. of ketone gave 54 g. of mercury compound. Recrystallized from ethyl alcohol, it melted at 134°.

Analyses. Calc. for C₁₉H₂₀O₄Hg: Hg, 39.1. Found: 39.3, 39.1.

α-Bromomercuri- β -methoxy- β -phenylpropiophenone.—To 25 g. of the acetate dissolved in alcohol was added drop by drop while the mixture was stirred exactly one molecular equivalent of potassium bromide dissolved in a little water. The bromide was precipitated as an oily product but solidified on standing. It was recrystallized from methyl alcohol; yield, 20 g.; m. p., 141°.

Analyses. Calc. for C₁₆H₁₅O₂BrHg: C, 36.94; Hg, 38.6. Found: C, 36.91, Hg, 39.3.

 α -Bromomercuri- β -ethoxy- β -phenylpropiophenone.—In a similar manner, the bromomercuri-ethoxy derivative was prepared by treating the acetate with one molecular equivalent of potassium bromide. The product, recrystallized from ethyl alcohol, melted at 138°.

Analysis. Calc. for C17H17O2BrHg: Hg, 37.6. Found: 37.7.

 α -Bromo- β -methoxy- β -phenylpropiophenone.—To 50 g. of the acetoxymercuric methoxy derivative of benzalacetophenone dissolved in methyl alcohol one molecular equivalent of bromine was added slowly while the mixture was stirred, and the flask containing the mercury compound was cooled with ice water. After a half hour most of the alcohol was removed by distillation and the residue dissolved in ether. The ethereal solution was washed several times with strong aqueous potassium bromide to remove mercuric bromide, and then with water. After evaporation of the ether an oil remained, most of which solidified on standing. Recrystallized from methyl alcohol, it melted at 76°.

Analysis. Calc. for C16H15O2Br: Br, 25.0. Found: 24.4.

α-Bromo- β -ethoxy- β -phenylpropiophenone.—The ethoxy compound was prepared in a similar manner by bromination of the ethoxy-mercury compound in alcohol or ether. Recrystallized from ethyl alcohol, it melted at 60–61°; 55 g. of mercury compound gave 18 g. of product.

Analyses. Calc. for $C_{17}H_{17}O_2Br$: C, 61.26; H, 5.10. Found: C, 61.49, 61.36; H, 5.18, 5.14.

The combustion of this compound was troublesome. When burned carefully in an ordinary combustion tube, a certain portion of material always came through undecomposed. It was necessary to use the cerium oxide-asbestos catalyst described by Reimer.¹¹

The compound melting at $60-6\frac{1}{2}$ ° (small needles) was always obtained except in the last run made when flat crystals melting at 74° resulted. This was evidently the other racemate possible.

Analyses (compound melting at 74°). Calc. for $C_{17}H_{17}O_2Br$: Br, 24.0. Found: 23.9, 24.2.

 α -Iodo- β -methoxy- β -phenylpropiophenone and the Ethoxy Compound.—Treatment of the mercury compounds with iodine instead of bromine gave the iodo-alkoxy addition products of benzalacetophenone.

The ethoxy compound melted at 75-76°.

Analysis. Calc. for C₁₇H₁₇O₂I: I, 33.4. Found: 33.4.

The methoxy compound melted at 96°.

Analysis. Calc. for C16H18O2I: I, 34.7. Found: 34.6.

¹¹ Reimer, This Journal, 37, 1636 (1915).

Action of Alkali on α -Bromo- β -methoxy- β -phenylpropiophenone and Addition of Mercuric Acetate to the Product.—A solution of 13.8 g. of the bromine compound in methyl alcohol was treated with one molecular equivalent of sodium methylate. The solution was heated until it became neutral. It was then poured into water and extracted with ether. The oil obtained from the ether layer was distilled at 6 mm. The fraction boiling at 200–205° was collected; yield, 8 g. The ethoxy compound was prepared in the same way, by the action of sodium ethylate on the α -bromo- β -ethoxy ketone.

The methoxy compound was dissolved in 90% methyl alcohol and treated with two molecular equivalents of mercuric acetate. As the solution stood, a white crystalline substance was gradually deposited. After 24 hours 80% of the calculated amount had crystallized. It was only very slightly soluble in alcohol; m. p., 237°. The analysis indicated that the product was the diacetoxymercuri derivative of dibenzoyl methane.

Analyses. Calc. for $C_{19}H_{16}O_6Hg_2$: C, 30.75; H, 2.14; Hg, 54.1. Found: C, 30.20; H, 2.21; Hg, 54.5, 54.6.

The ethoxy compound reacted with mercuric acetate in ethyl alcohol to give the same mercury compound, shown by analysis and by a mixed-melting-point determination.

A suspension of 10 g. of the compound melting at 237° in an excess of dil. hydrochloric acid was warmed until it had completely decomposed. The oil which remained was separated and crystallized from alcohol; yield, 90%. It melted at 80°, gave a red color with ferric chloride, and a copper derivative. A mixed-melting-point determination showed it to be dibenzoyl-methane.

Reaction of Ethylmagnesium Bromide with α -Bromomercuri- β -methoxy- β -phenyl-propiophenone.—The mercury compound was only very slightly soluble in ether, 5 g. was ground to a fine powder and added slowly to three molecular equivalents of ethylmagnesium bromide. A vigorous reaction took place. When all of the solid had been added, the clear solution was poured into ice water. The ether solution contained an oil which later solidified. It was recrystallized several times from alcohol to free it from mercury diethyl; m. p., 63°. The substance proved to be β -phenyl-valerophenone.

Analyses. Calc. for C₁₇H₁₈O: C, 85.7; H, 7.61. Found: C, 85.7; H, 7.54.

Reaction of α -Acetoxymercuri- β -alkoxy- β -phenylpropiophenone with Acids and with Potassium Iodide.—The mercury compounds were slowly decomposed by cold hydrochloric acid and rapidly by hot acid. The products were mercuric chloride and benzalacetophenone. When the mercury compounds were dissolved in alcohol and hydrogen sulfide was passed through the solution, there was an immediate precipitate of mercuric sulfide. The filtrate from the sulfide on concentration yielded benzalacetophenone. When boiled with an excess of aqueous potassium iodide, the mercury compounds were decomposed, the solution became alkaline and on cooling benzalacetophenone was recovered from the solution by extraction with ether.

Reaction of Dibenzalacetone with Mercuric Acetate.—To 5 g. of dibenzalacetone was added 13.6 g. of mercuric acetate in 100 cc. of absolute methyl alcohol. After 48 hours 15 g. of product had precipitated. Recrystallized from methyl alcohol, in which it is somewhat soluble, the compound melted at 183°. Analyses showed it to be the dimercurated compound, two methoxyl and two mercury groups having been added.

Analyses. Calc. for C₂₃H₂₆O₇Hg₂: C, 33.85; H, 3.21; Hg, 49.2. Found: C, 33.74; H, 3.10; Hg, 49.0, 49.2.

The acetoxymercuri-ethoxy derivative of dibenzalacetone was prepared by carrying out the reaction in ethyl instead of methyl alcohol. The acetate melted at 188-190°.

Analysis. Calc. for C25H30O7Hg2: Hg, 47.6. Found: 47.7.

 α -Acetoxymercuri- β -methoxy- β -phenyl-p-chloropropiophenone.—A solution of 10 g. of benzal-p-chloro-acetophenone and 13 g. of mercuric acetate in 300 cc. of absolute methyl alcohol, prepared by heating the mixture for a short time on the steam-bath, was allowed to stand several days, concentrated to 50 cc. and again allowed to stand, when about 50% of the mercury compound was slowly precipitated. Recrystallized from methyl alcohol, it melted at 124°.

Analysis. Calc. for C₁₈H₁₇O₄ClHg: Hg, 37.6. Found: 37.6.

Sodium chloride solution was added to the filtrate from the acetate and the chloride precipitated. Recrystallized from methyl alcohol, it melted at 160° .

Analysis. Calc. for C₁₆H₁₄O₂Cl₂Hg: Hg, 39.3. Found: 39.0.

Summary

- 1. The reaction of several α,β -unsaturated ketones with alcoholic mercuric acetate has been studied. The products obtained were saturated ketones formed by the addition of the groups —HgX and —OR to the double linkage.
- 2. The reaction of unsaturated ketones with mercuric acetate has been compared with that of mercuric halides.
- 3. Reactions and derivatives of the mercury compounds have been described.

CAMBRIDGE 38, MASSACHUSETTS

NOTES

Absorption of Halogens by Mercurous Salts: Preliminary Note.— The present work grew out of an attempt to make a more effective mercurial preparation for external application by treating calomel with iodine. In spite of the large amount of work which has been done on various complex mercuric compounds, the mixed mercuric salts, X—Hg—Y, have not been prepared by the action of halogens on mercurous compounds. During the present study, mercurous chloride, sulfate, and nitrate have been treated with alcoholic solutions of iodine and bromine in excess. Mercurous chloride yields mercuric iodochloride, HgICl, and mercuric bromochloride, HgBrCl. The sulfate yields di-iodomercuric sulfate, (IHg)₂SO₄, and a perbromide, (BrHg)₂SO₄.Br₂. The latter compound reacts with dry chlorine to give dichloromercuric sulfate, (CIHg)₂SO₄. The nitrate gives a per-iodide, (IHgNO₃)₂.I₂, and a perbromide, (BrHg-NO₃)₂.Br₂. The former compound, when treated with chlorine, differs from the corresponding sulfate by giving a perchloride, (CIHgNO₃)₂.Cl₂.

It is too early to discuss definitely the constitution of this series of compounds of mercury. They exhibit a number of interesting peculiarities

¹ Ditte, Compt. rend., 87, 794 (1879); 92, 353 (1881). Varet, ibid., 123, 497 (1896). Harth, Z. anorg. Chem., 14, 323 (1897). Dobrosserdoff, J. Russ. Phys. Chem. Soc., 33, 303, 387 (1901). Sherrill, Z. physik. Chem., 43, 705 (1903). Borelli, Gazz. chim. ital., 38, I, 361 (1908); 38, II, 421 (1908).

which are being actively studied by physicochemical means. The study of their therapeutic effects may lead to interesting developments. As they contain easily reactive halogen atoms, they might be useful in making other compounds of mercury, or in organic synthesis.

The experimental details of the preparation and properties of the substances, as well as the analytical data, will be published in a later paper on their constitution.

The Chemical Laboratories of the College Kuverji Gosai Naik,
Baroda, India Mahadeo Dattatraya Avasare
Received September 18, 1922

The Catalytic Bromination of Aliphatic Acid Chlorides.—The use of iron, ferric chloride, aluminum chloride, etc., in brominating and chlorinating aromatic compounds has found widespread application. In the aliphatic series, however, the use of iron as a catalyst in introducing bromine within the molecule has been limited chiefly to saturated and unsaturated hydrocarbons.

Meyer¹ and Kronstein² have presented a series of papers dealing with the bromination of hydrocarbons using iron as a catalyst. Willstätter and Bruce³ used iron powder in preparing 1,2-dibromocyclobutane, and recently Mereshkowsky⁴ has studied the ratio of reaction products obtained in the bromination of hydrocarbons and their bromine derivatives by using iron wire, ferric bromide, aluminum, and aluminum trichloride as catalysts. In brominating acetic acid and its homologs the use of sulfur as catalyst is well known.

During the course of researches on derivatives of camphoronic acid, $(CH_3)_2C(COOH)-C(CH_3)(COOH)-CH_2COOH$ (a description of which will appear later), it was found necessary to brominate anhydrocamphoronyl chloride, $C_6H_{11}(CO)_2OCOCl$. The bromination hitherto has been carried out by Bredt⁵ either by heating one or both isomers with bromine in a sealed tube at elevated temperatures, or in an open vessel on the waterbath, the reaction product being a mixture of two isomeric bromo-anhydrocamphoronyl chlorides in which it is known that the bromine is attached to the primary carbon atom of the molecule. The latter scheme required about 12 hours for complete reaction to take place.

The above procedure was modified by treating anhydrocamphoronic acid, C₆H_{II}(CO)₂OCOOH, formed in quantitative yields by heating pure, optically-active camphoronic acid under a vacuum at 180° in an oil-bath with 1.1 molecular equivalents of phosphorus pentachloride in a flask

¹ Meyer, Ber., 24, 4247 (1891); 25, 3304 (1892).

² Kronstein, Ber., 24, 4245 (1891); 26, 2436 (1893); 54, 1 (1921).

⁸ Willstätter and Bruce, Ber., 40, 3983 (1907).

⁴ Mereshkowsky, Ann., 431, 113 (1923).

⁵ Bredt, Ann., 299, 142 (1899).

bearing a ground-glass tube and condenser together with a separatory funnel sealed to its side. The mixture was warmed and when the reaction had ceased, without distilling the phosphorus oxychloride, a small amount of iron powder (0.2-0.5 g.) was added. Then, while the mixture was heated on the water-bath, 1.1 molecular equivalents of bromine was slowly added through the separatory funnel. A violent bromination of the camphoronyl chlorides followed. After all the bromine had been added the mixture was heated for 45 minutes to insure complete reaction. At the end of this time, when no fumes of bromine could be detected, the flask was removed and allowed to stand at room temperature for 24 hours to permit the crystallization of the α -bromo-anhydrocamphoronyl chloride. The contents of the flask were filtered and the crude product, obtained in yields of 75%, was repeatedly washed with small amounts of absolute ether to remove both its readily soluble isomer and ferric bromide. The solid was dissolved in hot benzene, boiled with Norite two or three times and finally allowed to cool. Transparent crystals of the pure product melting at 168° were obtained. The original filtrate contained some α -bromo acid chloride together with ferric bromide and the β -, or isomeric, bromo acid chloride. The latter compound has never been obtained in a pure state.

This method of catalytic halogenation appears to have considerable value in the catalytic preparation of α -halogen acids. It is the intention of the writer to continue investigation of the reaction, extending it not only to other acid chlorides, but also to other classes of aliphatic compounds to which it has not been applied.

CHEMICAL LABORATORY UNIVERSITY OF ILLINOIS URBANA, ILLINOIS Received July 23, 1923

WALTHER F. GOEBEL

The Purity of Alpha-Gamma-Dichlorohydrin Prepared by the Action of Hydrogen Chloride on Glycerol.—In the preparation of α, γ -dichlorohydrin from glycerol by the action of hydrogen chloride there is the possibility of forming considerable amounts of α, β -dichlorohydrin (the dichloride of allyl alcohol). The complete separation of such a mixture by distillation would be very difficult. In order to obtain information in regard to the purity of the dichlorohydrin prepared in this way, we investigated the action of p-nitrobenzoyl chloride on the final product of the reaction which was collected over a 3° range and over a 7° range. The preparation and distillation was carried out as described in "Organic Syntheses," Vol. II, p. 29. Five g. of the material was mixed with 20 g. of pyridine and 8 g. of p-nitrobenzoyl chloride; the mixture was heated for 3 hours on the steam-bath, then allowed to stand overnight and finally treated with dil. hydrochloric acid and extracted with ether. After the removal of nitrobenzoic acid by means of aqueous sodium carbonate, the ether

was dried and evaporated. From the 3° portion 10.2 g. of ester was obtained, m. p. $55-58^{\circ}$ (94% yield), and 10.0 g. from the 7° portion, m. p. $53-57.5^{\circ}$ (92% yield). The pure ester after several recrystallizations melted at $58-59^{\circ}$.

Calc. for C9H9O4NCl2: Cl, 25.5. Found: 25.4.

The isomeric ester of α,β -dichlorohydrin was made in a similar fashion from the allyl alcohol dichloride. It melted after several recrystallizations at $35.5-37^{\circ}$.

Calc. for C9H9NCl2: Cl, 25.5. Found: 25.7.

A mixture of 90% of the α,γ -ester and 10% of the α,β -ester melted at $26\text{--}48^\circ$. The crude product from the 3° and 7° portions must, therefore, have contained much less than 10% of the isomeric ester. Since the yields of this crude ester were 94 and 92%, the original portions must have contained at least 91% and 89% of α,γ -dichlorohydrin (assuming the melting points corresponded to 97% purity). Considering the losses in the manipulation, etc., it is probable that the purity is several per cent. higher than this; the relatively high melting point of the crude ester points to the almost complete absence of the α,β -dichlorohydrin from both portions.

CONTRIBUTION FROM THE CHEMICAL LABORATORY J. B. CONANT AND O. R. QUAYLE OF HARVARD UNIVERSITY

CAMBRIDGE 38, MASSACHUSETTS Received August 13, 1923

NEW BOOKS

The Phase Rule and the Study of Heterogeneous Equilibria: an Introductory Study. By A. C. D. RIVETT, D.Sc., Associate Professor of Chemistry in the University of Melbourne. Oxford University Press, American Branch, New York, 1923. 204 pp. 118 figs. 20 × 13 cm. Price \$3.50.

This little book by Professor Rivett is a welcome addition to our very limited textbook literature of the phase rule. Outside of Roozeboom's "Die heterogenen Gleichgewichte," which is too encyclopedic for any but a specialist, and Bancroft's "Phase Rule," which has had its greatest use in bringing to the attention of chemists the value of the phase rule at a time when it was but little known, there have been only two readable books on the phase rule, as far as the reviewer knows, which could be put in the hands of a graduate student or an investigator needing an acquaintance with the phase rule for the purposes of his research—namely, Findlay's, "Phase Rule" and Clibbens' "Principles of the Phase Theory." This third book fulfils the requirement of being another readable book—perhaps more so than Clibbens—and at the same time presents, in clear and understandable language much material that is not found in either of the others. The author states that it is not "either a treatise or a book of reference," but is intended as "an introduction to the subject." In the opinion of

the reviewer, it will be most valuable if used in conjunction with Findlay rather than as an independent introduction, since each of the texts supplements the other. Findlay, as pointed out by the author in his preface, has confined himself quite largely to the study of condensed systems, and Rivett has repaired that omission by giving us a most excellent development of one- and two-component systems including the vapor phase. The treatment of three-component and four-component systems is also complete to a degree that would hardly be expected in a book of but two hundred pages. It is of course a necessity that these things have been done by excluding some other things—and they are precisely the condensed systems which Findlay has treated so admirably. Each text supplements the other, and the pair give a much more satisfactory introduction than either alone.

Professor Rivett's book is written in a clear and logical style, which never leaves the reader in doubt as to his meaning. Diagrams and typography are also good. The reviewer feels that Professor Rivett would run less danger of losing a student's interest if he had used more specific examples in the text, even at the expense of some of the general discussion. Of the one hundred and eighteen phase-rule diagrams only a half dozen have specific components attached to them, and statistical data are not given for a single system. It would not be necessary to expand the book by very many pages in order to include enough data to convince the student who is being introduced to the phase rule via Professor Rivett's book that the rule works for real concrete systems made up of real chemicals.

ARTHUR E. HILL

Landolt-Börnstein Physikalisch-Chemische Tabellen (Physical-Chemical Tables). Fifth edition, revised and enlarged. By Dr. Walther A. Roth, Professor an der Technischen Hochschule, Braunschweig, and Dr. Karl Scheel, Professor an der Physik.-Techn. Reichsanstalt, Charlottenburg. Julius Springer, Linkstr. 23-24, Berlin W. 9, Germany. Two volumes, xvi + 1695 pp. 1 fig. 20 × 28 cm. Price \$45.00.

The new edition of these invaluable tables is very welcome. The last (fourth) edition appeared in 1912; eleven years is a long interim to be covered, at the present rate of growth of physics and chemistry.

The increased size of the present edition reflects this rapidity of growth. The new edition has nearly 1700 pages as compared with the 1300 pages of the old edition. A number of entirely new chapters have been added, dealing with radioactivity, spectrum analysis, electric phenomena in gases, the physics of the atom, and crystal structure, while the old chapters, particularly those dealing with the critical state, with electromotive forces, and with solubility, have been very greatly enlarged. A further addition is a special index covering the properties of the most important and best-known common substances.

Both of the original editors are now dead, so that we owe the present edition to Walther A. Roth, Karl Scheel, and half a hundred German collaborators.

These volumes, like their predecessors, constitute a splendid achievement. At least until our new International Critical Tables shall have appeared, they will be indispensable to every investigator or laboratory engaged upon research in physical or chemical science. To be sure, they do not present all the data for the various constants treated and frequently, extracts only are given of many important modern data, but in the great majority of cases these extracts should be adequate and, if they are not, the references to the original sources are available. The data, too, have not been as critically examined as might be desired, and the index is far too small and too poorly cross-referenced for so large and multifarious a subject matter. However, to have collected and arranged such a colossal number of data so carefully and so well, and to have printed them so clearly and indeed beautifully, merit our admiration and gratitude.

This new edition can also be looked upon as one more forward step in the resumption of the orderly progress of science in Germany.

ARTHUR B. LAMB

Les Isotopes (Isotopes). By Professor A. Damiens, of the Faculty of Pharmacy, Paris. Gauthier-Villars, Quai des Grands-Augustins, 55, Paris, 1923. ix + 118 pp. 33 figs. 25.5 imes 16.5 cm. Price 12 fr.

It may well occasion some surprise, in view of the uniquely authoritative nature of Aston's treatise on this subject, as well as its eminently readable character, that another author has thought it worth while to prepare a book of almost the same size covering nearly the same field, and bearing the same title.

This surprise can only increase when it is learned that Aston's "Isotopes" has recently appeared in French translation. The present author, however, has recognized that since most of the progress in this field has been made by physicists, it is they who have taken in hand the enlightenment of the general scientific public as to the results of their labors. The vast theoretical importance of these results to chemistry makes it desirable that the experimental evidence in the case should be collected and critically examined by an open-minded chemist, and subsequently presented for the examination of others in such detail and with such a marshalling of facts that no critical student need feel the necessity of accepting any longer the ready-made opinions of workers in other fields as to the importance to him of the phenomenon of isotopy.

This task has been well performed. The book in parts is very complete. Many of the crucial experiments, as well as the confirmatory researches which followed them, especially the more recent ones, are reported with a

wealth of experimental detail, cuts, and documentation such as one would hardly expect to find in a summary treatise of this sort. With sound judgment the author has condensed the section on radioactivity and positive rays, probably in view of the excellent accounts of this field already published, and has correspondingly amplified his examination of the atomic weight work, the partial separations of isotopes, and the researches on such properties as melting point, density, index of refraction, etc., which lend themselves to comparative "large-scale" study.

The book seems relatively free from serious errors or omissions, considering the author's lack of experience in these rather special domains of investigation, but the discussion of the radioactivity of the atomic weight samples of active lead (pp. 36-37) is not especially luminous proportionality between radioactivity and atomic weight, found by Richards and his co-workers, is presumably due (a) in some of the minerals to an admixture of thorium lead; (b) possibly to a partial decay of the radium-D content after the separation of the lead from the mineral; and (c) in some cases perhaps to an accidental admixture of traces of radium-D in the preliminary preparation of the sample. A failure to make the measurements under strictly comparable conditions might also be suspected, except that the activities of differently purified samples of the same mineral show excellent agreement. The author seems troubled by a remark of Richards and Wadsworth to the effect that the radioactivity of their specimens was due to radium-E. It is obvious that the measurable β -ray activity of a pure radium-D preparation which has been left for 20 or 30 days is always due almost solely to radium-E, however completely this product may have been "removed in the preliminary purification." The length of the half-life of Ra-D (24 years) is hardly a reason for surprise at this conclusion. It does not seem quite true (p. 55) that in attempting to separate isotopes one should always employ at the start only materials of the highest purity. Among minor slips of the pen one notes "plomb" for "baryum" on the last line of p. 1, and COCl2 for COCl on pp. 93 and 111.

In addition to being valuable as a compilation, the book is interesting for the assumption which is its principal excuse for being, namely, that a worker in one field may profitably attempt a comprehensive criticism of the methods and conclusions in another. In this case the author is to be commended for the good will and thoroughness with which this task has been attempted. He does well to emphasize again the axiom that when one tries to display minute differential effects, nothing but the most elaborate recital of precautions, purifications and tests can be convincing. Nor has one very important point escaped him. Two different states of mind have animated the workers in this field,—one group has experimented with a view to the confirmation of preconceived theories, others have only sought to make numerous and precise measurements, with minds freed from the

start, of all premature conceptions. Brilliant and important advances have resulted from both methods of work.

NORRIS F. HALL

La Technique Industrielle des Parfums Synthétiques (The Industrial Technique of the Manufacture of Synthetic Perfumes). By René Sornet. Gauthier-Villars, 55, Quai des Grands-Augustins, Paris, 1923. x + 135 pp. 14.5 × 22.5 cm. Price, unbound, 10 fr.

Although the manufacture of synthetic perfumes is a comparatively new industry a great deal has already been accomplished in this branch of applied science, and it represents a field of research which still continues to attract the attention and interest of chemists in many lands. It is well known that France has long occupied a leading position in the cultivation of flowers from which some of the most delicate perfumes are obtained, and that the consequent development in that country of the art of perfumery has led to the establishment of very large industries. An impetus was thus given to the systematic investigation of these floral products and also of the so-called essential oils from other sources, many of which are used in perfumery. As a result of such studies it has been found possible to produce by synthetical methods many of the more important odorous substances occurring in nature, and these achievements have led to a very great expansion of the perfume industry. It has furthermore been observed that a large number of definite organic compounds which have not as yet been found to occur in nature possess such fragrant properties as to render them of value in the manufacture of perfumes and they are now extensively utilized for this purpose. The literature in this particular domain of chemical science has consequently become very voluminous, and many patents have been issued for the protection of individual products. These considerations appear to have suggested the compilation of the little volume under notice, which is specially designed to supply the technical information that is not to be found in the various textbooks of organic chemistry or in those laboratory manuals which more specifically describe the methods for preparing organic compounds. It may be noted, however, in this connection that it was not the purpose of the author to include any information concerning the composition or manufacture of finished perfumes, which are usually of a complex nature.

The subject matter of the present work is divided into five parts which comprise, respectively, the alcohols, aldehydes, ketones, esters, and substances of diverse character such, for example, as coumarin and musk. Under each of these divisions a number of compounds are described, together with the reactions which take place in their formation, and there are some citations of current literature. The work is concisely written and, although limited in its scope, will doubtless be found of value to those who are interested in the industrial production of synthetic perfumes.

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THE CRYSTAL STRUCTURE OF MAGNESIUM STANNIDE

By Linus Pauling Received May 21, 1923

Introduction

The temperature-composition diagram¹ of the binary system, magnesiumtin, shows a pronounced maximum corresponding to the composition Mg₂Sn. This compound is described² as cubic with octahedral habit and complete octahedral cleavage. For the purpose of obtaining information regarding the nature of intermetallic compounds, crystals of magnesium stannide, Mg₂Sn, have been investigated by means of X-rays, resulting in a complete determination of their structure. No crystal structure determination for an intermetallic compound has been previously reported.

By melting the calculated amounts of magnesium and tin in an iron crucible under a mixture of potassium and magnesium chlorides, and cooling slowly, a mass of magnesium stannide was obtained from which individual crystals could be cleaved. The X-ray data were obtained from Laue and spectral photographs, treated as described by Dickinson.³ I wish to express my thanks to Dr. Roscoe G. Dickinson for his advice and active interest in this research.

The Determination of the Structure

Spectral data from a (111) face of a crystal of magnesium stannide are given in Table I. Using the value of 3.591 for the density,² these data place $n^3/m = 0.248$ for the first reflection. No reflections were found on the Laue photographs with values of $n\lambda$ less than 0.26 Å. U., calculated for the unit containing four Mg₂Sn, with n = 1, and $d_{100} = 6.78 \pm 0.02$ Å. U.

- ¹ Kurnakow and Stepanow, Z. anorg. Chem., 46, 177 (1905).
- ² Sustschinsky, Z. Krist., 38, 265 (1904).
- ³ Dickinson, This Journal, 44, 276 (1922).

As the lower limit of X-rays present in the spectrum was 0.24 Å. U., a larger unit of structure is not indicated.

A symmetrical Laue photograph through the (111) face showed a trigonal axis and three reflection planes; consequently only arrangements derived from point-groups $T_{\rm d}$, O and O_h were treated. No planes but those with all indices odd gave values of $n\lambda$ less than 0.50, although a large number of other planes were in positions favorable for reflection, so treatment was given only to arrangements based on a face-centered lattice. There are three ways⁴ of arranging $4Mg_2Sn$ with these restrictions, irrespective of any assumptions regarding the equivalence of atoms of one element. These are

The intensity of the third order (111) reflection is greater than that of the second order, and the structure factor, $S = \sqrt{A^2 + B^2}$, must be greater for the third order. For Arrangements II and III, the corresponding values are

$$n=2$$
, $A=4\overline{Sn}$, $B=0$; $n=3$, $A=4\overline{Sn}-4\overline{Mg}$, $B=\pm 4\overline{Mg}$.

On the very safe assumption that an atom of tin scatters X-rays more strongly than an atom of magnesium, the value of S for the third order is less than that for the second order, eliminating these two arrangements.

For Arrangement I reflecting planes may be divided into three classes, which have the following values of S.

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Class I: hkl one odd, two even; n=1, S=0; n=2, S=4\overline{\text{Sn}}-8\overline{\text{Mg}} Class II: hkl all odd; n=1, S=4\overline{\text{Sn}} Class III: hkl two odd, one even; n=1, S=0; n=2, S=4\overline{\text{Sn}}+8\overline{\text{Mg}}.
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On the previously made assumption regarding relative reflecting powers, the values for the structure factor of the classes of planes increase in this

Table I

Reflection Data for Mg₂Sn, (111) Face

X-rays reflected Å. U.	Angle of	<u>d111</u> n Å. U.	7	
A. U.	reflection	A. U.	$I_{\mathtt{observed}}$	S
$Mo\beta_1 = 0.6311$	4° 37′	3.918	strong	4Sn
$Mo\alpha_1 = 0.7078$	5° 11′	3.921		
$Mo\beta_1$	9° 16′	$^{1}/_{2} \times 3.920$	weak	4Sn - 8Mg
$Mo\alpha_1$	10° 26′	$^{1}/_{2} \times 3.913$		· ·
$Mo\beta_1$	14° 3′	$^{1}/_{3} \times 3.899$	medium	4Sn
$Mo\alpha_1$	15° 46′	$^{1}/_{3} \times 3.913$		
$Mo\beta_1$	18° 52′	$^{1}/_{4} \times 3.902$	medium	$4\overline{\text{Sn}} + 8\overline{\text{Mg}}$

⁴ Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Carnegie Inst. Pub., 1922.

order: I, II, III. Intensity data showing the extent of the agreement with this structure are given in Tables I and II. In comparing intensities of two planes reflecting at the same wave length, if the intensity of the plane with the smaller value of d/n is larger than that of the other, the structure factor of the first must be greater than that of the second. No intensity relations not accounted for by the above arrangement were observed.

Table II Laue Photographic Data for ${\rm Mg_2Sn.}$ Incident Beam 12° 30' from Normal to (111)

	\mathbf{d}_{kkl}					\mathbf{d}_{kkl}			
hkl	Å. U.	Å. U.	Iobserved	Class	hkl	Å. U.	Å. U.	I_{observed}	Class
$13\overline{3}$	1.52	0.28	2.8	II	$41\overline{2}$	0.74	0.29	0.08	Ι
$\overline{112}$	1.38	.30	8	III	$91\overline{3}$.71	.32	.3	II
$\overline{5}11$	1.30	.31	2.4	II	771	.68	.34	.2	II
$\overline{1}5\overline{3}$	1.15	.36	2.4	II	$50\overline{1}$.67	.33	.4	III
$30\overline{1}$	1.07	.33	2.6	III	$\overline{1}9\overline{5}$.66	.28	.14	II
$03\overline{2}$	0.94	.33	0.5	I	$05\overline{2}$.63	.45	.4	1
$2\overline{3}1$.91	.26	.4	III	$\overline{11}.1.\overline{1}$.61	.32	.12	II
$35\overline{5}$.88	.26	.2	II	$11.1.\overline{1}$.61	.46	.5	II
$71\overline{3}$.88	.31	.6	II	$11.1.\overline{3}$.59	.31	.10	II .
$\overline{3}7\overline{3}$.83	.30	.5	II	$\overline{4}33$.58	.48	1.0	III
$17\overline{5}$.78	.30	.4	II					

Discussion of the Structure

The structure determined for magnesium stannide is the one known as the calcium fluoride arrangement.⁵ It places eight magnesium atoms around each tin atom at the corners of a cube, and four tin atoms around each magnesium atom at tetrahedron corners. The sum of the atomic radii of magnesium⁶ and tin⁷ obtained from the distance between atoms in the metals is 3.01 Å. U. (from gray tin) or 2.80 (from white tin); the closest approach of tin and magnesium atoms in magnesium stannide is 2.94 ± 0.01 . There is no similarity in the way in which an atom of tin or magnesium is surrounded by other atoms in the metals and in this compound.

Crystals of sodium cadmide, NaCd₂, reported from goniometrical measurements as cubic, were prepared by the method of Kurnakow.⁸ Each of several Laue photographs taken from three different crystals with the beam perpendicular to an octahedral face showed a 3-fold symmetry axis lying in three symmetry planes. The photographs were, however, so complicated that it was not found possible to assign indices with certainty to many of the spots even on the symmetrical photographs. It was accordingly not possible to determine the apparently very complex structure.

W. H. and W. L. Bragg, Proc. Roy. Soc., 89A, 474 (1913).

⁶ Hull, Phys. Rev., [2] 10, 661 (1917).

Bijl and Kolkmeier, Proc. Acad. Sci. Amsterdam, 21, 494 (1919).

⁸ Kurnakow, Z. anorg. Chem., 23, 459 (1900).

In view of the lack of a simple valence relation between the atoms, complex atom-groups may be formed in sodium cadmide in a way similar to the formation of Pb_2^- ions in a solution of sodium plumbide, $NaPb_2$, in liquid ammonia, preventing a simplicity of structure.

Summary

Crystals of the intermetallic compound magnesium stannide, Mg₂Sn, have been prepared and investigated by means of Laue and spectral photographs with the aid of the theory of space-groups. The intermetallic compound has been found to have the calcium fluoride structure, with $d_{100}=6.78\,\pm\,0.02$ Å. U. The closest approach of tin and magnesium atoms is $2.94\,\pm\,0.01$ Å. U.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE THEORY OF EMULSIFICATION1

By Philip Finkle, Hal D. Draper and Joel H. Hildebrand Received June 6, 1923

To disperse one liquid in another in the form of an emulsion requires the doing of work upon the system equal to the product of the interfacial tension multiplied by the increase in surface. An emulsion produced by the mechanical agitation of two pure, incompletely miscible liquids is, therefore, always unstable, the drops of dispersed liquid coalescing upon contact to decrease the interfacial area. To stabilize an emulsion a suitable third substance must be added. Many very effective emulsifiers are known but there has been thus far no altogether satisfactory way to predict the relative powers of different emulsifying agents, either to stabilize the emulsions or to determine which of the two liquids shall be dispersed in the other. Some very useful criteria yielded by experience are more in the nature of rules than theories. We will refer to some of these briefly and then proceed to elaborate an hypothesis which seems to account for the behavior of all emulsifying agents for which we have the data to apply it.

To form a stable foam or emulsion requires that the films of enclosing liquid which separate the bubbles or drops, respectively, shall be stable. This cannot be the case with a pure liquid, since a film represents a surface which is far from the minimum possible. It was shown by Rayleigh that a film is stabilized by the addition of some substance which, by virtue of high adsorption at the surface, greatly lowers the surface tension. In such a case the surface tension is larger at a fresh surface than at an old surface, at which there has been time for the adsorption to take place by diffusion,

Kraus, This Journal, 29, 1557 (1907).

¹ Presented at the Colloid Symposium held at Madison, Wis., in June, 1923, under the auspices of the Department of Chemistry of the University of Wisconsin.

so that if an old surface is threatened with rupture, the new surface thereby formed is stronger than the old, and further strain is diverted from the threatened point. This is the effect of soap in stabilizing the water films between the bubbles in soap suds. Since the globules of dispersed liquid in an emulsion must likewise be held apart by a stable film of the enclosing liquid, the presence of a solute which is highly adsorbed at the interface stabilizes the film and prevents the coalescence of the drops. Thus, soap, which is adsorbed at a water-oil surface as well as at a water-air surface, stabilizes a water-oil emulsion as it does a water-air "emulsion." The difficulty enters when we consider the difference in the type of the emulsion produced by soaps of the alkali metals on the one hand, which disperse the oil in the water, and heavier metal soaps on the other hand, which disperse the water in the oil, for we have adsorption and lowering of the interfacial tension in both cases, and might expect either an oil or a water film to be stabilized.

Bancroft² connects the type of emulsion with the phase which is the best solvent for the emulsifying agent. He says,

"If the adsorption of the emulsifying agent lowers the surface tension on the water side of the interface more than it does on the oil side, the interface will tend to curve so as to be convex on the water side, and we shall have a tendency to emulsify oil in water. If the adsorption of the emulsifying agent lowers the surface tension on the oil side of the interface more than it does on the water side, the interface will tend to curve so as to be concave on the water side, and we shall have a tendency to emulsify water in oil. The simplest way, then, to emulsify oil in water is to add a water-soluble colloid which is adsorbed strongly at the interface and the simplest way to emulsify water in oil is to add an oil-soluble colloid which is adsorbed strongly in the interface."

The idea of a film with two surface tensions, one on the oil side and another on the water side, is rather disconcerting, for no one is likely to measure separately the surface tensions on two sides of an interface, and we have evidence, furthermore, that the emulsifying agent may form films at the interface which are but one molecule thick.³ The general rule which this theory implies, that the external phase is the one which is the best solvent for the emulsifier is undoubtedly true in most instances. Thus, the alkali metal soaps are soluble in water and disperse oil in water, while the soaps of iron, zinc, aluminum, etc., which are more soluble in benzene and other solvents of low polarity, disperse the water in the other liquid. A contradiction exists, however, in the case of a fatty acid, such as oleic acid, which, though soluble in benzene and not in water, gives an unstable emulsion of benzene in water.

Bhatnagar,4 on the basis of considerable experimental data, has arrived

² Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1922.

³ Langmuir, (a) Met. Chem. Eng., 15, 468 (1916); (b) This Journal, 39, 1848 (1917); (c) Adam, Proc. Roy. Soc. London, 99A, 336 (1921); (d) 101A, 452 (1922); (e) Griffin, This Journal, 45, 1648 (1923).

4 Bhatnagar, J. Chem. Soc., 119, 61, 1760 (1921).

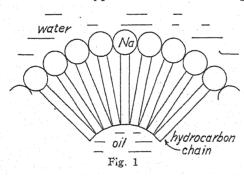
at what may likewise be regarded as a rule rather than a theory. "All emulsifying agents having an excess of negative ions adsorbed on them and wetted by water will yield oil-in-water, emulsions, while those having an excess of adsorbed positive ions and wetted by oil give water-in-oil emulsions."

The role played by the orientation of the molecules in the interface in determining the direction of curvature was suggested by Langmuir,^{3a} who said,

"This theory also affords an explanation of the mechanism by which colloids are formed. If a film of closely packed oleic acid molecules covers the surface of water to which sodium hydroxide has been added, OH group are adsorbed by the COOH radicals, causing an expansion of the lower side of the film without a corresponding expansion of the upper side. This results in the bulging of the film downwards in spots so that it finally detaches itself in the form of particles, the outer surfaces of which consist of COOH groups together with the adsorbed OH, while the interior consists of the long hydrocarbon chains.

"The size of the colloidal particles is determined by the difference in size between the two ends of the molecules, just as the size of an arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed."

Harkins, Davies and Clark⁵ applied essentially the same view to explain the reversal of type in emulsions conecting the differences between sodium



and potassium oleates as emulsifying agents with the number of oleate radicals in the molecule of the soap.

It is possible to test the orientation hypothesis in a very striking way in the case of the soaps, where the work of Langmuir and of Harkins and co-workers seems amply to justify the assumption that at an interface between

water and some liquid of low polarity, such as benzene, any soap would form an interfacial film, which might be as little as one molecule thick, whose molecules would be oriented with the non-polar hydrocarbon chain in the benzene and the polar metallic end in the water.

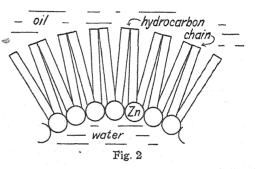
Now, if the polar group, in the water, occupies more space than is necessary for the closest packing of the hydrocarbon chain, the latter can be packed more closely if the film is convex on the water side, as illustrated in Fig. 1, in a highly idealized form. It is obvious that the direction and degree of curvature, if this hypothesis is correct, should vary, first, with the atomic volume of the metal, being more convex the larger this volume, and second, with the number of hydrocarbon chains attached to a

⁵ Harkins, Davies and Clark, This Journal, 39, 354, 541 (1917).

single metallic atom, according to its valence. Zinc soap, for example, would correspond to Fig. 2, making the interface convex towards the "oil" side; while an aluminum soap should give still more curvature and more stable emulsions of water in oil. Where the cross section of the hydrocarbon chain and of the metallic end are of the same magnitude, there will be no tendency to curvature, and no very stable emulsion, in spite of the high adsorption at the interface which is still possible.

The relative sizes of the metallic atoms in the various soaps may be inferred from the atomic volumes of the metals, and from their atomic

diameters in the free state and in compounds. Values are given in Table I. The atomic diameters are according to Hull, Bragg, and Richards, respectively. Of course, hydration may modify the effective atomic domain, but since, for example, the hydration of silver ion can hardly be as great as that of sodium ion, this fac-



tor may be expected to increase rather than to oppose the effect of the differences evident in Table I.

Application of the theory to these figures would indicate that the ability of soaps of calcium, potassium, sodium and silver to emulsify oil in water would

Table I Relative Sizes of Atoms

		mic diamete		
Element	In metal Hull	Bragg	Richards	Atomic volumes
Cs	• • • • •	4.75	3.8	70.6
K		4.15	3.46 (in K	(Cl) 45.3
Na	3.72	3.55	2.85 (in N	aCl) 22.9
Ag	2.87	3.55		10.3
Ca	8.93	3.40	••	12.6
Mg	3.22	2.85		7.0
Zn	2.67	2.65	••	4.6
Al	2.86	2.70		3.4
Fe	2.48	2.80	a de la compania	2.3

decrease in the order given; or, viewed from the other angle, their ability to emulsify water in oil should increase in this order; that the soaps of the divalent metals, calcium, magnesium and zinc, should have much less

⁶ Hull, Proc. Am. Inst. Elec. Eng., 38, 1171 (1919); Science, 52, 227 (1920).

⁷ Bragg, Phil. Mag., [6] 40, 169 (1920).

⁸ Richards, This Journal, 45, 422 (1923).

ability to emulsify oil in water or much greater ability to emulsify water in oil, and further, that they should vary in these respects in the order given. The soaps of the trivalent metals aluminum and iron, should exhibit the greatest tendency to emulsify water in oil. The values in the several columns for the relative sizes of iron and aluminum atoms do not all agree, so that the relative emulsifying powers are not definitely indicated by these figures. In general, the values for the atomic diameters of the free metals are most reliable, since the values for the atomic diameters in compounds involve two variables which require some further consideration for their determination. On the other hand, there may be doubt that the elementary atom with its electrons occupies the same domain as does the atomic kernel in the compounds. However, there are enough uncertain factors involved to deter us from attempting to make any very fine distinctions on the basis of existing figures for atomic diameters.

To confirm the difference between the volumes of the metallic end of the molecule in Na and Ag soaps we made approximate determinations of the molecular volumes of their stearates as follows.

Molecular Volumes in Saturated Solutions

St	earate	Acetone	Benzene	Methyl alcohol	Av.
	Na	338	330		334
	Ag	309		291	300

There were known, previous to our own study of this subject, some facts which support this theory of the action of soaps. The soaps of the alkali metals are very effective in stabilizing oil-in-water emulsions, potassium soaps being more effective than sodium soaps. Magnesium soaps emulsify water in oil, 10 salts of the trivalent metals, aluminum and iron, are especially effective in reversing oil-in-water emulsions stabilized by soaps of the alkali metals. Emulsions of oil in water stabilized by sodium oleate are reversed by adding magnesium, aluminum, ferrous or ferric salts in amounts chemically equivalent to the sodium oleate used. 11

These facts encouraged us to undertake a more systematic study of the applicability of the theory here outlined. Stearates and oleates of the metals listed in Table I were used to prepare several series of emulsions, in which the concentrations of soap, the relative amounts of oil and water used and the degrees of shaking were varied for the different series, but composed of equivalent amounts of soaps in any one series. One liquid was always water, the other benzene, xylene or hexane.

Each group of emulsions was placed in a thermostat maintained at 23° and the time noted when each emulsion began visibly to break down.

⁹ Neunier and Maury, Collegium, 1910, 277; Chem. Zentr., 1910, II, 1416.

¹⁰ Newman, J. Phys. Chem., 18, 34 (1914).

¹¹ Parsons and Wilson, J. Ind. Eng. Chem., 13, 1116 (1921).

Table II gives the results of a typical series. Other series using stearates in place of oleates, and still others using xylene or hexane in place of benzene gave results so entirely in accord with those here given that their

TABLE II

Types and Stabilities of Emulsions									
	Dispersed	l phase, l	Benzene		Disp	persed p	hase, Wa	ter——	
Oleate of	Cs	K	Na	Ca	Ag	Mg	Zn .	Al	Fe
Approx, life of emuls.	8 wk.	8 wk.	6 wk	1 hr	1.4	2.4	24 d	7 A	10 A

detailed reproduction is hardly necessary. The correspondence in all cases was far more closely in accord with the theory than we had dared to anticipate.

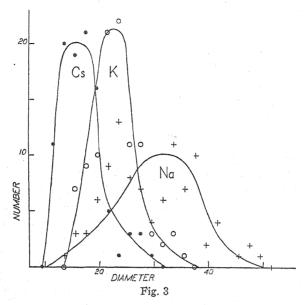
The results in these cases are also in accord with the rule that the external phase is the one which is the better solvent for the emulsifier. The soaps of the alkali metals are more soluble in water, the others more soluble in the non-polar liquid. The soaps of iron and aluminum have more symmetrical and less polar molecules and would, therefore, be expected to dissolve best in solvents of low polarity, while the alkali-metal soaps, consisting of a single chain with a highly polar end, cannot dissolve considerably in non-polar liquids but can, on the other hand, form clusters with the hydrocarbon chains in the interior, which can then dissolve "colloidally" in water.

If the orientation theory is correct, the different degrees of curvature natural to films of different soaps should yield drops of different sizes. Since the shaking would never produce drops of uniform size in any emulsion, it was necessary to determine the distribution of a large number of drops between different size intervals. (To take the mean size would obviously give abnormal weight to the occasional very large drops.) A micrometer microscope was used, and the diameter of all drops in the field measured, the field being altered often enough to get a total of 100 drops. The operator did not know which emulsion he was measuring until after he had finished.

Four different series of emulsions with cesium, potassium and sodium stearates were thus measured, the conditions in all series being identical except for the kind of soap used. Table III and Fig. 3 represent the results with one series. The size intervals are represented in scale divisions of the microscope micrometer, of which $60~{\rm div.}=0.01~{\rm mm.}$ The other series showed a similar displacement of the maxima, although due to differences in shaking, etc., among the different series, the soap did not yield the same maximum each time.

The flatness of the curve for sodium stearate in Fig. 3 evidently has no significance in view of the relatively small number of drops counted. In the other series no such marked difference occurred.

It is evident from these data that the cesium soap gives the smallest drops and the sodium soap the largest, so that the curvatures of the films actually differ in the predicted direction and, therefore, support the theory.



Many powdered solids have been shown to be capable of stabilizing emulsions.¹² It seems to be possible to account for the type of emulsion

Table III
Relation of Drop Size to the Kind of Soap Used

Size interval	Cesium	No. of drops Potassium soap	Sodium	Size interval	Cesium soap	No. of dr Potassiu soap	m Sodium soap
9-10	0	0	0	31-32	0	2	6
11-12	11	0	0	33-34	0	3	11
13-14	20	0	1	35–36	0	1	7
15-16	19	7	3	37-38	0	0	10
17-18	21	9	3	39-40	0	0	2
19-20	16	10	6	41-42	0	0	4
21-22	5	21	9	43-44	0	0	0
23-24	1 -	22	13	45 - 46	0	0	1
25-26	3	11	8	47-48	0	0	2
27-28	3	11	7	49-50	0	0	1
29-30	1	3	4				

produced by the following hypothesis. It is obvious, first, that the powder must collect at the interface in order to be effective. Now, this will occur

¹² Compare Pickering, J. Chem. Soc., 91, 2010 (1907); Kolloid Z., 7, 11 (1910). Sheppard, J. Phys. Chem., 23, 634 (1919). Schlaepfer, J. Chem. Soc., 113, 522 (1918). Moore, This Journal, 41, 940 (1919).

only when the solid is wetted by both liquids, with a finite angle of contact of the interface with the solid. In general, one liquid will wet the solid better than the other, as represented in Fig. 4, so that the particles will be drawn more largely into the former. If there are enough solid particles to fill the interface the tendency of the interface to contract will cause it to bend, as shown in Fig. 4, in the direction of the more poorly wetting liquid, which makes it easy for the latter to become the enclosed phase. Of course, a solid, in order to behave in this way, must be easily dispersed in the outer liquid, its particles not tending to agglomerate therein or to stick together when serving as protective armor for emulsified drops. One should, therefore, be able to predict whether or not a given solid powder can stabilize an emulsion, and also which liquid will become the

dispersed phase, by noting the angle of contact of the interface with the solid. Data upon this point are not abundant but seem to be altogether confirmatory, and a microscopic examination of an emulsion of water in benzene stabilized by lampblack confirmed the picture given in Fig. 4.

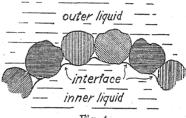


Fig. 4

We suggest that this picture may serve to explain the Bancroft rule that a colloid emulsifier causes the phase in which it is soluble to be external. A colloidal particle with only a few polar groups upon it would remain largely in the oil phase and vice versa, so that the natural curvature of the surface may be determined in much the same way as with powdered emulsifiers.

Summary

- The present status of the theory of emulsification has been outlined.
- The types and relative stabilities of emulsions formed by the aid of various soaps have been explained by the aid of the theory of orientation of the soap molecules in the interface.
- 3. The curvature of the film of soap adsorbed at the interface is more convex toward the water, yielding more stable emulsions of the oil-enclosed type, the larger the metal atom in the soap.
- 4. As the number of hydrocarbon chains attached to a single metallic atom increases (with the valence of the metal) the curvature is reversed, becoming strongly convex towards the oil phase with soaps of the trivalent metals, aluminum and iron, which yield the most stable emulsions of water in oil.
- 5. Experimental data upon the type and relative stabilities of emulsions of various liquids with water show that the transition from the most stable oil-enclosed to the most stable water-enclosed emulsion for both stearates

and oleates follows the order: cesium, potassium, sodium, calcium, silver, magnesium, zinc, aluminum, iron. This order is in accord with the valences and atomic diameters of the metals, as interpreted by the orientation theory.

6. It is suggested that the type of emulsion produced by a solid powder is determined by the angle of contact of the interface with the solid. In order for the powder to remain in the interface the angle must be finite, and unless the angle is 90°, the interface will be on one side or the other of the points of contact of the particles, and its tension will cause the film to be concave on that side.

BERKELEY, CALIFORNIA

[Contribution from the Chemical Laboratory of Clark University, I, 35]

DISPLACEMENT OF METALS FROM SOLUTIONS OF THEIR SALTS BY LESS ELECTROPOSITIVE ELEMENTS

I. THE REPLACEMENT OF SODIUM AND POTASSIUM BY MAGNESIUM AND ALUMINUM

By F. W. BERGSTROM¹

RECEIVED JUNE 22, 1923

Introduction

Franklin² found that a solution of potassium amide in liquid ammonia reacts readily with magnesium to form an opaque blue solution, which disappears within a few hours leaving a precipitate of the sparingly soluble potassium ammono-magnesiate, Mg(NHK)₂.2NH₃.³ During the preparation in an analogous manner of potassium and sodium ammono-aluminates the author observed the production of similar intermediate blue solutions. The present work, which was undertaken primarily for the purpose of accounting for the phenomena observed, and of establishing the equations for the reactions, is a portion of a general investigation dealing with the action of potassium and potassium amide upon the elements.

- ¹ National Research Council Fellow.
- ² Franklin, This Journal, 35, 1463 (1913).
- ³ Potassium and sodium amides are bases of the ammonia system, and behave in this solvent just as potassium and sodium hydroxides behave in water. Thus an aqueous solution of potassium hydroxide dissolves aluminum and zinc to form, respectively, potassium aquo-aluminate and potassium aquo-zincate, while a liquid ammonia solution of potassium amide dissolves aluminum to form a potassium ammono-aluminate, and reacts with zinc to form a sparingly soluble potassium ammono-zincate. Potassium ammono-magnesiate, on the other hand, has no analog in the water system, because the much greater solvolytic power of water relative to that of ammonia renders its existence impossible. Reactions thus occur in ammonia that cannot take place in water. For a further explanation of the ammonia system of acids, bases and salts, see Am. Chem. J., 47, 285 (1912); Proc. Eighth Int. Cong. Appl. Chem., 6, 119 (1912).

Discussion of the Reactions

The alkali and alkaline earth metals dissolve abundantly in liquid ammonia, yielding intensely colored blue solutions, which on concentration acquire a beautiful coppery luster. This behavior is characteristic of solutions of these elements alone, and so may be regarded as a positive test for their presence. Magnesium, if its surface is perfectly clean, dissolves to a slight extent in liquid ammonia, the saturated solution being light blue and readily transparent. Amalgamated aluminum does not dissolve under ordinary conditions, but might be expected to do so to a much less extent than magnesium if the surface were continually kept clean and free from amide as, for instance, by the action of a solution of sodium or potassium amide.

It is plain, therefore, that the opaque blue solutions obtained by the action of potassium amide on magnesium and aluminum, and of sodium amide on aluminum, must contain free alkali metal, for the strong color cannot possibly be due to either of the less electropositive elements. As a further and confirmatory test, these solutions, when evaporated almost to dryness, were found to assume the familiar coppery color characteristic of concentrated solutions of the alkali metals. After complete removal of the solvent, rather imperfect crystals of sodium or potassium were found to be deposited upon the walls of the reaction tube.

Kraus⁴ has shown that dilute solutions of the alkali metals in liquid ammonia conduct the electric current in the same manner as ordinary salts. The positive carrier is the sodium ion, Na⁺, while the negative carrier is the solvated negative electron, which may be represented by the symbol e⁻. The conductance curve in these regions is similar in form to the curves obtained with solutions of the common salts, approaching asymptotically a limiting value as the dilution increases.⁵

In view of these facts one should expect dilute solutions of the alkali metals to exhibit salt-like properties in other respects. In fact, Kraus⁶ has shown that the following metathetic reaction readily takes place because of the low solubility of one of the products, calcium chloride, in liquid ammonia: Ca (dslvd.) + 2KCl (dslvd.) = CaCl₂(ppt.) + 2K (dslvd.).

Magnesium⁷ is slightly soluble in ammonia, while aluminum probably dissolves under the proper conditions to a much less extent. Accordingly when either of these metals is treated with sodium or potassium amide, most of its ions are removed from solution by formation of the very slightly soluble magnesium or aluminum amide, and we have a virtual

- 4 Kraus, This Journal, 43, 749 (1921), and previous articles.
- ⁵ At a concentration above about 0.5 N, metallic conduction causes the curve to rise rapidly, a saturated solution conducting the current as well as many metals.
 - ⁶ Kraus, ibid., 44, 1224 (1922).
 - ⁷ Cottrell, J. Phys. Chem., 18, 96 (1914).

metathesis, which may be represented by the equations: $Mg + 2KNH_2 \longrightarrow Mg(NH_2)_2 + 2K$; Al + $3NaNH_2 \longrightarrow Al(NH_2)_3 + 3Na$.

In view of the slight solubility of both magnesium and aluminum, and in view of the fact that their amides cannot be completely insoluble, although, being weak bases, they must be but very slightly ionized in solution,⁸ it is necessary to assume an equilibrium to exist. This is being continually displaced toward the right because of the interaction of the alkali metal solutions with the solvent, in which process magnesium and aluminum play the part of catalytic agents: $3K + 3NH_3 \longrightarrow 3KNH_2 + \frac{3}{2}N_2$; or $3Na + 3NH_3 \longrightarrow 3NaNH_2 + \frac{3}{2}H_2$.

Aluminum and magnesium amides are both amphoteric in their properties and therefore react with the excess of potassium or sodium amide present to give the ammono salts finally obtained. In this manner aluminum and magnesium ions are practically completely removed from solution and the equilibrium is further displaced toward the right. The complete equations for the formation of sodium ammono-aluminate may then be written: Al + $3NaNH_2 \longrightarrow Al(NH_2)_3 + 3Na$; Al $(NH_2)_3 + NaNH_2 = Al(NH_2)_2NHNa.NH_3$; $3Na + 3NH_3 = 3NaNH_2 + \frac{3}{2}H_2$; and for the formation of potassium ammono-magnesiate: $Mg + 2KNH_2 \longrightarrow Mg(NH_2)_2 + 2K$; $Mg(NH_2)_2 + 2KNH_2 \longrightarrow Mg(NHK)_2.2NH_3$; $2K + 2NH_3 \longrightarrow 2KNH_2 + H_2$.

In view of the relative rapidity of formation of potassium ammono-aluminate and magnesiate, and of sodium ammono-aluminate according to the above type equations, it is probable that the equilibria of which the first equation is an example rest far over on the right hand side. In the first example above, sodium amide has a solubility of approximately 1 g. per liter, ^{8a} yet the blue solution obtained on interaction with aluminum is quite opaque and contains sodium in fairly high concentration.

Evidence for the intermediate formation of aluminum amide has been obtained during a previous study of the action of potassium amide on aluminum. Aluminum, although a very reactive metal, is quickly covered in air with an adherent protective coating of oxide which hinders further action. Consequently in order that reaction with the alkali metal amides might take place at all, it was necessary to amalgamate the surface. It will be shown later that the mercury plays no essential part in the course of the reactions, although it may in some measure increase the velocity.

This work suggests that the reactions between potassium or sodium hydroxide and aluminum may partially take place in an analogous manner,

⁸ Even the relatively strong ammono bases, sodium and potassium amides, are ionized only to a small extent in solution. Nevertheless, aluminum and magnesium amides are weak enough to exhibit amphoteric properties toward them. Kraus, "Properties of Electrically Conducting Systems," 1922, p. 59. American Chemical Society Monograph, Chemical Catalog Co.

⁸s E. C. Franklin, unpublished work.

that is, the evolution of hydrogen may be due to a secondary action of potassium or sodium on water rather than to a direct replacement of the hydrogen of the hydroxyl group. Certain experiments already carried out favor this view, but further discussion will be reserved for a future paper.

Action of Solutions of Sodium and Potassium on Aluminum

Potassium⁹ and sodium ammono-aluminates are formed by the action of solutions of the alkali metals alone on amalgamated aluminum. It seems probable that the potassium or sodium is first converted to amide by the combined catalytic action of the aluminum and mercury, and this in turn reacts as previously described. It was found, curiously enough, that the formation of sodium ammono-aluminate by either of the methods mentioned was two to three times more rapid than the formation of the potassium analog, undoubtedly because of difference in the rapidity of the initial stage of the reaction.

Potassium amide, due to its superior solubility, probably reacts at first much more rapidly on aluminum, quickly coating the amalgamated areas over with a thick and relatively adherent layer of aluminum amide and preventing for the time being direct contact between portions of the metal and the solution. Experiments^{9a} with potassium amide and slightly amalgamated aluminum have shown that the amalgamated surfaces may be covered up so as to stop the reaction completely, although only temporarily, causing a periodic production and disappearance of the blue potassium solution. With sparingly soluble sodium amide, aluminum amide is undoubtedly formed at a slower rate, and thus has no tendency to form a retarding layer, that is, contact exists between the active areas of the metal and solution at all times. The resultant reaction is, therefore, more rapid.

That the mercury is inert, aside from possible catalytic effects, is shown in the two following experiments.

- (1) A piece of sheet aluminum was well amalgamated in a liquid ammonia solution of mercuric iodide, ¹⁰ washed with the same solvent, and then sealed up in one leg of a two-legged reaction tube. ¹¹ The other leg contained a few tenths of a gram of sodium. Ammonia was distilled into the reaction tube, a portion of the sodium solution was poured upon the aluminum and allowed to remain until the mercury of the amalgam was saturated, after which the metal strip was washed and allowed to remain in contact with fresh solvent for a day. No evidence of the formation of sodium ammono-aluminate could be obtained, even after the mercury had been treated again with sodium.
- (2) A moderately concentrated sodium amalgam was prepared by agitating a solution of sodium in liquid ammonia with mercury in a three-legged reaction tube. This together with the ammonia was then poured upon a small, well-amalgamated slab of

³ (a) Unpublished work of the Author. (b) See C. A., 16, 3822 (1922).

¹⁰ To prevent oxidation.

¹¹ See Expt. 4.

aluminum prepared as in the preceding experiment. At the end of $4^{1}/_{2}$ months no sodium ammono-aluminate had been formed.

Sodium Ammono-Aluminate

Sodium ammono-aluminate, obtained by either of the methods mentioned, is readily soluble in liquid ammonia at ordinary temperatures, and may be obtained in the form of small white needles by cooling a moderately concentrated solution to $-40^{\circ}.^{12}$ The solubility at 0° is only a little less than at room temperature. Curiously enough, large crops of blunt prisms were obtained in two cases by cooling (in ice water) the solution obtained immediately after the disappearance of the blue color of the sodium. After these solutions had stood for a day, only the small needles, previously described, were obtained when the liquid was cooled to -40° . The existence of two crystalline modifications of this salt is not surprising in view of the fact that aluminum cyanide behaves in a somewhat similar manner. 9a

Sodium ammono-aluminate when dried in a vacuum at either -33° or room temperature corresponds in composition to $Al(NH_2)_2NHNa.NH_3$, $Al(NH_2)_3.NaNH_2$ or $Na[Al(NH_2)_4]$. When heated in a vacuum it melts near 90° with a large increase of pressure, giving off one molecule of ammonia and forming $Al(NH_2)_2.NHNa$, a solid of the nature of a glass, and possessing no crystalline structure.

Water reacts very vigorously with either of the above compounds, a great deal of heat being developed. The resulting products of hydrolysis are for the most part soluble in the water introduced into the reaction tube. Hydrochloric acid then reacts with this solution of sodium aquo-aluminate and with the remaining precipitate to form aluminum, ammonium, and sodium chlorides.

Experimental Part

The general methods used for the preparation of compounds in liquid ammonia solution and their subsequent analysis have been described in previous articles.¹³

In this work analyses were made on aliquot portions of the hydrochloric acid solution of the specimen.

Preparation 1.—In one leg of a two-legged reaction tube were placed 0.35 g. of sodium and an excess of commercial sheet aluminum, the other leg remaining clean and empty for subsequent crystallization of the aluminate. The sodium was completely converted after 24 hours into a colorless solution of sodium ammono-aluminate, which was then separated from a small quantity of residue by decantation into the other leg. On cooling to 0°, a large crop of blunt thick needles was obtained, although only the fine needles could be isolated in the succeeding experiments. When this stood for a day.

¹² In an open ammonia bath.

¹³ This Journal, **27**, 831 (1905); **29**, 1694 (1907); **35**, 1460 (1913). *J. Phys. Chem.*, **15**, 915 (1911); **16**, 694 (1912).

partial ammonolysis took place with the deposition of some amorphous white precipitate. Accordingly, the solution was merely evaporated to dryness and then analyzed.

. Analyses. Subs., dried in a vacuum at -40° (1–2 mm.), 1.3055 g. Wt., dried in a vacuum at room temperature, (1 mm.), 1.3053 g. One-fifth gave 0.1650 g. of sodium sulfate; two-fifths gave 0.2346 g. of Al₂O₃.

Preparation 2.—The reaction between 0.34 g. of sodium in the form of amide with an excess of pure amalgamated aluminum was complete at the end of a day. The resulting salt was crystallized once by cooling the moderately concentrated solution in an open liquid-ammonia bath, and ammonia of crystallization at —33° was determined by the method outlined by Franklin. Unfortunately, a small quantity of sodium amide lodged in the stopcock tube and could not be removed, helping to make the sodium analysis run a little high. The analytical results for the first and fourth experiments are more satisfactory, even though impure aluminum was used. The larger surface of metal exposed in these cases undoubtedly accounts for the facts.

Analysis. Subs., dried in a vacuum at -33° , 0.9335 g. Wt., dried in a vacuum at room temperature, 0.9323 g. Two-fifths gave 0.1633 g. of Al₂O₅; one-fifth gave 0.08989 g. of nitrogen; one-fifth gave 0.0813 g. of Al₂O₃ and 0.1026 g. of NaCl.

Preparation 3.—The preparation was carried out as in Expt. 1, using, however, small pieces of pure amalgamated aluminum. The sodium solution was changed to sodium ammono-aluminate within a day. The product was crystallized twice at —40° without the appearance of insoluble ammono basic residues. (Compare Expt. 1.) On heating in a vacuum, the salt melted at 85–90° and on continued evacuation finally solidified to a voluminous froth.

Analysis. Subs., dried in a vacuum at room temperature, 0.7736 g. Wt., heated in a vacuum at 110°, 0.6528 g. (Probably a little overheated.) One-quarter gave 0.06929 g. of nitrogen; one-quarter gave 0.0879 g. of Al₂O₃ and 0.1032 g. of NaCl.

Preparation 4.—This experiment was performed primarily to see whether the mercury of the amalgam took any essential part in the reaction. After completion of the tests described previously in this article, the sodium solution was poured upon the aluminum, and allowed to react with it. The salt was crystallized twice at 40°, then dried in a vacuum at room temperature and 105°.

Analysis. Subs., dried in a vacuum at room temperature, 1.0004 g. Wt., dried in a vacuum at 105°, 0.8513 g. One-quarter gave 0.1145 g. of Al₂O₃ and 0.1274 g. of NaCl; one-quarter gave 0.09206 g. of nitrogen. One-quarter gave 0.1147 g. of Al₂O₃.

SUMMARY OF ANALYSES

Dried in a	vacuum	at —33°	or room	tempe	rature.	Heated	in a va	icuum a	above 1	00°
Cale.sf A1(NH2)2NH		No. 1	Found No. 2	No. 3	No. 4	Calc. Al(NH	for 2)2NHNa	Found No. 3	No. 4	
Al	23.7	23.8	23.1	24.0	24.2	A1	27.9	28.5	28.5	
N	49.2		48.2	48.7	49.1	N	43.3	42.4	43.3	
Na	20.2	20.5	21.6	21.0	20.0	Na	23.7	24.9	23.6	

In conclusion the author wishes to thank Dr. Charles A. Kraus for his kind and helpful interest in this work.

Summary

1. Sodium amide and amalgamated aluminum react to form a definite crystalline compound, sodium ammono-aluminate, to which any one of the following formulas may be given: Al(NH₂)₂NHNa.NH₃, Al (NH₂)₃.NaNH₂,

or Na[Al(NH₂)₄]. This compound loses one molecule of ammonia on heating in a vacuum above 90°. The equations for the reaction have been shown to be Al + 3NaNH₂ \longrightarrow Al(NH₂)₃ + 3Na; Al(NH₂)₃ + NaNH₂ = Al(NH₂)₂NHNa.NH₃; 3Na + 3NH₃ = $\frac{3}{2}$ H₂ + 3NaNH₂.

The action of potassium amide on amalgamated aluminum and on magnesium are analogous in character. An explanation is given which depends upon the fact previously pointed out by Kraus that dilute solutions of the alkali metals in ammonia are salt-like in character. The initial stages may be regarded as metatheses, although actually involving equilibria which suffer continual displacement because of secondary reactions.

2. A solution of sodium in liquid ammonia reacts with amalgamated aluminum to form the same sodium ammono-aluminate described above. Sodium amide is probably first formed, and this in turn reacts according to the equations given. The mercury of the amalgam does not play an essential part in the reaction.

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[Contribution from the Chemical Laboratory of Johns Hopkins University]

THE DIELECTRIC CONSTANTS OF ORGANIC LIQUIDS AT THE BOILING POINT

By F. V. Grimm and W. A. Patrick Received June 29, 1923

The following study was undertaken with the idea of finding some relationship between the dielectric constant of liquids and other physical properties. It was thought that the dielectric constant would be found to be related to those properties of liquids that depend upon the force of molecular attraction, namely, latent heat of vaporization, surface tension, etc. That such relationships do exist is shown by the parallelism that is exhibited in the case of organic homologs. 1,2,3 The conclusion was, however, reached that no simple relationship exists between the dielectric constant and the latent heat of vaporization although in the case of closely related liquids there was unmistakable evidence to show that the contrary is true. Walden4 connects several physical properties of liquids with the following function of the dielectric constant: $\frac{D.C.-1}{D.C.+2}$, $\frac{1}{\delta}$ which according to the Clausius-Mossotti theory involves the volume actually occupied by the molecules. All of these relations give different values for associated and non-associated liquids. Walden uses values of surface tension, latent heat of vaporization, etc., at the boiling temperature, while the values of

¹ Hesehus, Physik. Z., [2] 750 (1900).

² Campbell, "Modern Electrical Theory," Cambridge University Press, 1913.

³ Obach, Phil. Mag., [5] 32, 113 (1891). ⁴ Walden, Z. physik. Chem., 70, 569 (1910).

the dielectric constant and density are taken at 20°. This procedure was justified on the ground that according to the Clausius-Mossotti theory the above function is independent of the temperature. However, Katz⁵ has shown that the function in question is not independent of the temperature but gives variations that are especially marked with liquids of high dielectric constant.

If we accept the classical electronic theory of dielectrics, we arrive at the following picture: the dielectric constant is due to a displacement of a certain number of electrons by the electric field. The following relation is given by Lorentz and Lorenz as expressing the connection between the dielectric constant and the number of displaced electrons N, the charge on an electron e and the force f due to the positive charge of the molecule which tends to restrain the electron from leaving.

D.C. =
$$1 + \frac{4\pi Ne^2}{f - \frac{4}{3\pi} Ne^2}$$

Thus we have two unknown quantities, N and f; N is probably proportional to the number of molecules and therefore to the density of the substance, but little or nothing is known of the force f. It is probable that this force is connected with the force of molecular attraction, and hence the relation that is sought between the dielectric constant and surface tension or latent heat of vaporization.

It has been suggested that more constant relations might be obtained if values of the dielectric constant were taken at the boiling temperature. This has been attempted by Turner⁶ with a few liquids by calculating the dielectric constant at the boiling point from the values at 20° and the temperature coefficient. However, the dielectric constant is not a linear function of the temperature, as has been shown by Katz and others, and in certain cases behaves in a most irregular manner. For example, Tangl⁷ has shown that the dielectric constant-temperature curve for ether is first convex and then concave toward the temperature axis. For this reason we have therefore undertaken to determine directly the dielectric constant at the boiling temperature. Thirty-five organic liquids in all were measured, and the results should be of the greatest value to anyone interested in the theory of dielectrics.

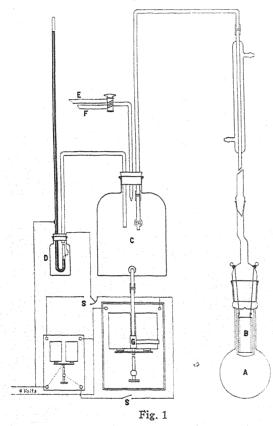
Measurements of the dielectric constant at the boiling point are not easily made due to the troublesome effect of conductivity, which increases very rapidly with increasing temperature. The method used in the following measurements has enabled us to work with liquids having a conductivity less than that of pure water, without sacrificing the accuracy of the results.

⁵ Katz, Z. physik. Chem., 19, 94 (1896).

⁵ Turner, J. Chem. Soc., 107, 276 (1915).

¹ Tangl, Drude's Ann., 10, 748 (1903).

Apparatus.—The method employed was a modification of the Nernst bridge method which has been described in detail by King and Patrick.⁸ With the exception of a different arrangement of the dielectric cell, very few changes in the apparatus were necessary. The dielectric cell consisted of two coaxial platinum cylinders sealed in a fixed position by small plugs of glass at both ends. This condenser was suspended in the liquid by means of two platinum wires. The size of the cylinders of cell No. 1 were 6.3×1.9 cm., and 6.3×2.2 cm. With this cell we were able to read changes of about forty in the dielectric constant. In using cell No. 2, in which the plates were closer together (the outer



cylinder was 2.1 cm. in diameter) the same change on our reference scale corresponded to a change of about ten in the dielectric constant. This latter cell could only be used with non-associated liquids or at least with liquids of low conductivity.

The liquid dielectric was brought to its boiling temperature by being immersed in a bath of its own vapor at a pressure of 760 mm. This pressure was held constant to within less than 1 mm. by means of a pressure regulator. The boiling flask (A) in Fig. 1 had a capacity of about 250 cc. and the dielectric cup 50 cc.; consequently, the minimum amount of liquid required for a determination was approximately 150 cc. The glass cup was suspended within the neck of the flask by means of four prongs, which allowed the vapor to pass around the cup into the condenser above. The cell (B) was suspended within this cup by two platinum wires sealed in at the top of the ground-glass stopper. Care had to be taken to prevent superheating of the

vapors surrounding the dielectric cup. The reading was taken when the liquid in the cup had reached such a temperature that an occasional bubble would rise from the bottom. This very slow boiling did not affect the location of the minimum, since the bubble did not pass between the two plates. This was found to be the criterion of the correct boiling temperature by a preliminary experiment in which the platinum cell was replaced by a standard thermometer and the boiling temperature of water observed.

By means of a slight bend in the tube leading from the flask to the condenser, it was possible, by giving the condenser a half turn in the ground-glass joint, to cause the refluxing liquid to drop directly into the cup or to run down the side of the flask as desired. This arrangement was to allow for refilling the cup in case an appreciable amount

⁸ King and Patrick, This Journal, 43, 1835 (1921).

of the liquid had evaporated before the final reading was obtained. The liquid was never allowed to reflux into the cup while a bridge reading was being taken, since this resulted in a shifting of the minimum due to the cooling effect of the condensed liquid.

The top of the condenser was connected to the equalizing bottle C of the manostat by means of glass tubing. The liquid was protected from the moisture of the air by a tube containing phosphorus pentoxide connected inside the bottle C. At the top of the equalizing bottle was a glass tube which could be connected either to the compressed air line or to a water suction pump at E and F. A third tube was connected with a bottle D containing the open end of a barometer. The mercury valve G of the gas regulator was attached to the bottom of the equalizing bottle.

The mercury in the barometer was so adjusted that when contact was made with the platinum wire sealed in at the lower limb, the height was exactly 760 mm. The barometer was calibrated both by determining the pressure at which pure water boiled at 100° and also by comparison with a standard barometer. When the atmospheric pressure was less than 760 mm., the system was connected with the pressure lines, and the electric connections were made as shown in the drawing. Thus when the circuit was broken between the mercury meniscus and the platinum point, the valve G opened and allowed the air to escape. By careful regulation of the air entering and leaving, the fluctuations of the mercury meniscus were reduced to less than 0.5 mm. In the case that the atmospheric pressure was greater than 760 mm. the system was connected to the reduced-pressure sides, and the second relay thrown in by means of the switches S and S'. We were therefore able to bring the pressure to the value 760 mm. under all conditions of atmospheric pressure. The two relays were actually enclosed in a double walled box not shown in the drawing. This was to prevent the noise of the relays from interfering with the location of the minimum on the bridge.

Calibration.—The calibration of the scale was made by using different standard liquids whose dielectric constants at room temperature were accurately known. The temperatures of the standard liquids were ascertained by allowing them to come to the temperature of the room in contact with a standard thermometer. The temperature was taken immediately before and after the bridge reading was made. The values of the known dielectric constant when plotted against the scale reading of the measuring condenser gave an exact straight line as shown by King and Patrick. This curve was plotted on a large sheet of paper (100×150 cm.) accurately coördinated in millimeters from which the values of the dielectric constant at the boiling temperature were taken. The standard liquids, the values of the dielectric constant at 18°, and the temperature coefficients are given in Table I.

Table I
DIELECTRIC CONSTANTS OF STANDARDS

Liquid	D. C. at 18°	$\frac{1}{D} imes \frac{\mathrm{d}D}{\mathrm{d}T}$	Observer
Benzene	 2.288	0.0007	Turner
Chloroform	 4.95	.00376	Walden
Aniline	 7.115	.00351	Katz and Turner
o-Nitrotoluene	 27.71	. 0055	Turner
Nitrobenzene	 36.45	.005	Turner

The scale of the measuring condenser was calibrated at frequent intervals during the course of this work and was tested with one or more standard liquids before and after each measurement.

Purification of Liquids

Benzene.—c. p. Benzene was shaken repeatedly with sulfuric acid until the latter was no longer darkened. It was then shaken with mercury, washed with water, dried

and distilled. After two fractional crystallizations, it was dried over metallic sodium and distilled. A constant-boiling fraction was preserved.

Chloroform.—After standing for several weeks over coned. sulfuric acid, the chloroform was washed repeatedly with water, dried over calcium chloride and fractionated. A 500cc. fraction which distilled within 0.03° was preserved.

Aniline.—c. P. Aniline was twice fractionally distilled, then crystallized, dried with potassium hydroxide and again distilled. A 400cc. fraction boiling within 0.15° was taken.

o-Nitrotoluene.—A c. p. sample was dried with calcium chloride, fractionated once by distillation and twice by crystallization, and finally redistilled. A 300cc. fraction boiling within less than 0.1° was taken.

Nitrobenzene.—c. p. Nitrobenzene was dried with phosphorus pentoxide. A fraction boiling at 212.0-212.08° (770 mm.) was used.

The standard liquids were kept in the dark in a desiccated atmosphere under a bell jar. They were several times redried and redistilled during the course of this work.

The liquids investigated were purchased in the purest possible condition and were further purified with suitable reagents, dried, and finally subjected to one or more fractional distillations, either at normal or reduced pressures. A very efficient all-glass still, consisting of six sections of a Young "evaporator," was used. The fractions taken, boiled within a small fraction of a degree of the correct temperatures, except of those of quinoline and acetonitrile. Quinoline which had been separated from any contained nitrobenzene by steam distillation and from aniline by diazotization and subsequent steam distillation, extracted with ether, distilled, and dried over potassium hydroxide, was subjected to several fractional distillations. Nevertheless, a constant-boiling fraction could not be obtained. The fraction finally used, consisted of about 200 cc., boiling between 237.3° and 238.5° (uncorr.).

Acetonitrile was washed with water, salted out with potassium hydroxide, dried and fractionally distilled several times with phosphorus pentoxide. The fraction used boiled at 80.1–81.3°. The liquid in the dielectric cell, however, probably represents a much better sample, since the first portion only was used in the cell.

The impurity which gave by far the most trouble was water. As is well known, it is very difficult if not impossible to remove the last traces of water from certain alcohols, ketones, etc., and the presence of a very small amount will increase the conductivity of these liquids to such an extent that a minimum on the bridge cannot be obtained. Even when the liquid had a very small conductivity at room temperature, it was often the case that at the boiling temperature the conductivity was so great that it required the maximum conductance of the shunt resistances to counterbalance it.

Fleming⁹ points out that there are two kinds of conductance: The first follows Ohm's law and is due to a large extent to impurities. This conductance can be greatly reduced if not eliminated entirely by proper purification and drying. The other conductance which does not obey Ohm's law, but is proportional to the frequency of the alternations, is caused by a slipping of the displaced electrons. This latter conductance increases very rapidly with the temperature, and because of this fact accurate measurements of the dielectric constant of certain liquids at the boiling temperature cannot

Fleming, Proc. Phys. Soc., [2] 23, 117 (1911).

be made. The values for acetonitrile, benzyl cyanide, ethylene chlorohydrin and nitromethane reported below have been rendered less accurate because of this conductivity.

The values of the dielectric constant at room temperature are included in Table II merely for comparison. They are reported in the first place only since no particular care was taken in their determination. The reason

TABLE II

Dielectric	CONST	ANTS OF	Liquids		
Liquid	D. C	C. at g point	В. Р . °С.	D. C. at room	temp.
Benzene	2.17	0.01	80.15	Standard (7	
Toluene	2.17	.01	110.70	2.3	24
<i>m</i> -Xylene	2.15	.01	139.3	2.4	24
p-Cymene	2.27	.02	176.5	2.5	25
Chloroform	4.23	.01	61.20	Standard	
Carbon tetrachloride	2.10	.01	76.74	2.2	23
Carbon disulfide	2.58	.01	46.25	2.6	25
Ethyl bromide	8.81	.02	38.40	9.4	24
Ethylene bromide	4.09	.02	131.3	4.8	2 3
iso-Amyl bromide	4.70	.02	120.6	6.1	25
n-Butyl iodide	4.52	.02	129.9	6.15	25
Methyl iodide	6.48	.02	42.35	7.0	24
Ethyl ether	4.11	.01	34.54	4.3	24
Ethyl acetate	5.30	.02	77.15	6.4	25
Chlorobenzene	4.20	.02	132.00	5.6	25
Aniline	4.54	.02	184.55	Standard	
o-Toluidine	4.00	.02	199.7	6.4	26
Acetonitrile	26.2	.10	81.60	36.2	25
Benzyl cyanide	8.5	.10	233.5	18.7	27
Butyraldehyde	10.78	.02	77.0	13.4	26
Paraldehyde	6.29	.02	128.0	13.9	25
Anisaldehyde	10.38	.02	248.0	22.3	22
Acetone	17.68	.02	56.15	21.0	21
Methylethyl ketone	14.46	.02	79.60	18.45	23
Acetophenone	8.64	.02	202.0	17.75	24
Ethylene chlorohydrin	13.2	.1	132.0	25.8	24.5
Ethyl alcohol	17.30	.02	78.32	25.8	20
n-Propyl alcohol	11.83	.02	97.19	20.8	23
n-Butyl alcohol	8.19	.02	117.71	17.8	25
iso-Amyl alcohol	5.82	.02	131.6	15.3	23
o-Nitrotoluene	11.82	.02	222.3	Standard	
Nitrobenzene	15.61	.02	210.85	Standard	1.0
Pyridine	9.38	.02	115.50	13.3	25
Nitromethane	27.75	.10	101	39	
Quinoline	5.05	.02	238	9.00	25

for this was that the temperature could not be determined accurately without exposing the liquids to the moisture of the air, which would result in a much higher conductivity and in certain cases would have prevented measurement being made at the higher temperature. It may be mentioned

here that it was necessary to distil several of the alcohols, ketones and nitriles directly into the flask A in order to prevent them from being contaminated with the moisture of the air.

When cell No. 1 was used, each millimeter of the scale division of the measuring condenser represented a change in the dielectric constant of nearly 0.02, and with cell No. 2 each scale division corresponded to a change in dielectric constant of 0.01. When the conductivity was not greater than that which could be balanced out with the shunt resistance filled with Mangani solution, ¹⁰ the readings could be checked to within less than one division.

In case the conductivity was greater than this, it was necessary to add potassium chloride to the Mangani solution in the shunt resistance tubes. As a consequence the greater part of the current was shunted around the condensers and the result was that the minimum became very much fainter. This was the case with the 4 liquids in Table II where the dielectric constant was determined to within only 0.1 of a unit. In no case are values reported which could not be checked within 5 scale divisions. The few liquids worked with which could not be determined with this precision were methyl alcohol, which had too high a conductivity and showed anomalous absorption, ethyl sulfate and monochlorohydrin.

Discussion of Results

It may be stated at the outset that no improvement in the empirical formulas of Walden and others was shown after the substitution of our results for the dielectric constant at the boiling point. The agreement was no worse than that obtained by Walden, but on the other hand it was no better. From this fact one may be inclined to agree with Walden that the particular function of the dielectric constant employed by him was independent of the temperature. However, it is our belief that no generalization connecting the dielectric constant with other properties of liquids has been formulated that is worthy of serious consideration. There is hardly another property of liquids which at a corresponding temperature exhibits such wide variations as the dielectric constant. The primary object of this paper is to provide accurate data which may serve as a basis for a physicochemical generalization regarding the dielectric constant of liquids.

In those expressions which contain the Clausius-Mossotti relation, the difference in the values when applied to associated liquids is probably due to the fact that the expression, $\frac{D.C.-1}{D.C.+2}$, is not a correct measure of the

volume actually occupied by the molecules. Furthermore, the assumption made by Lorentz that the molecules around a given molecule act with equal

 10 Mangani solution is prepared by dissolving 121 g. of mannite, 41 g. of boric acid and 0.06 g. of potassium chloride in one liter of water. This solution has a specific conductivity of 0.9 \times 10 $^{-\prime}$ and practically no temperature coefficient.

force upon it does not seem to be entirely justifiable. According to recent theories of the structure of the molecule, certain portions have stronger external fields than others. Such a theory is used by Langmuir in his explanation of surface energy, adsorption, etc. Likewise, the dipole theory of Debye¹¹ leads to the same conclusion. This theory attempts to explain the electrical properties of dielectrics on the assumption that in addition to the free and elastically bound electrons, there are electrical doublets or dipoles whose strength does not depend on the electric field in which they are situated. These dipoles are assumed to be the result of dissymmetry in the molecule. The theory cannot be said to be in its final form, although a recent modification by Gans¹² seems to hold great promise.

When we arranged liquids according to their value of the expression (D.C.-1)/(D.C.+2) it was found that the order did not agree with the known solubility relations or chemical properties. On the other hand, it was found by trial that the expression $\frac{(D.C./\delta)-1}{(D.C./\delta)+2}$ gave results of some value.

We therefore decided to use this latter expression as representing the volume actually occupied by the molecules.

The application of the above idea may be illustrated by applying it as a correction to Dieterici's equation for the internal heat of vaporization. Dieterici¹³ has shown that the empirical relation, $\lambda_i = CRT \log{(V_2/V_1)}$, where C is a constant, V_2 and V_1 are the specific volumes of the saturated vapor and liquid, respectively, and R is the ordinary gas constant referring to 1 g., holds over a wide range of temperature for normal or non-associated substances. When we substitute the free space of the molecules in the liquid state in place of V_1 , we obtain an equation similar to that of Bakker, ¹⁴ namely, $\lambda_i = CRT \log{(V_2/(V_1 - b))}$. We, however, set b equal to $\frac{(D.C./\delta) - 1}{(D.C./\delta) + 2}$

In Table III are given the values of the constant \mathcal{C} as calculated from the above equation. It is surprising to notice the constancy of \mathcal{C} even in the case of associated liquids. We do not claim that we are able to express exactly the actual volume occupied by the molecules in the liquid state, but some progress is indicated and it is predicted that further work along this line may reveal results of the greatest interest. A knowledge of the structure of liquids would certainly be of the utmost service in the elucidation of the many problems in the field of solutions, etc. It is interesting to note that the only liquids giving widely diverging values of \mathcal{C} are the ketones and compounds containing nitrogen.

¹¹ Debye, Physik. Z., 13, 97 (1912).

¹² Gans and Isnardi, ibid., 22, 130 (1921).

¹³ Dieterici, Ann. Physik, 25, 269 (1908).

¹⁴ Bakker, Z. physik. Chem., 12, 670 (1893).

TABLE III

LATENT HEATS OF VAPORIZATION AND MOLECULAR FREE SPACES						
Liquid	$\lambda_i + RT/M$	δat b. p.	b	C		
Benzene	94.4	0.8111	0.358	1.5		
Toluene	83.55	0.7781	.373	1.5		
m-Xylene	78.25	0.7572	.376	1.5		
Chloroform	58.4	1.4101	.400	1.5		
Carbon tetrachloride	46.4	1.4802	.123	1.6		
Ethylene bromide	43.6	1.932	.272	1.5		
Ethyl bromide	58.6	1.413	.636	1.3		
Butyl iodide	46.5	1.430	.418	1.6		
Ethyl ether	88.4	0.6968	.620	1.5		
Carbon disulfide	83.8	1.223	.270	1.4		
Aniline	104.3	0.8736	.583	1.45		
Pyridine	101.4	0.883	.762	1.3		
Ethyl acetate	83.1	0.8302	.642	1.4		
Nitrobenzene	81.7	1.0071	828	1.2		
o-Nitrotoluene	75.2	0.9603	.790	1.3		
Acetone	125.3	0.751	.882	1.3		
Methylethyl ketone	103.44	0.732	.864	1.3		
Ethyl alcohol	216.4	0.741	.882	1.5		
Butyl alcohol	134.3	0.727	.774	1.6		
iso-Amyl alcohol	120.9	0.715	.681	1.7		
iso-Amyl bromide	53.8	1.07	.532	1.5		
Chlorobenzene	73.7	0.9816	.522	1.45		
o-Toluidine	95.1	0.788	.576	1.5		
Quinoline	82.2	0.923	.598	1.4		
Acetophenone	77.24	0.8528	.752	1.3		
Nitromethane	114.8	1.03	.896	1.0		
Acetonitrile	173.6	0.7155	.922	1.0		
Paraldehyde		0.873	.675	1.5		
Propyl alcohol		0.736	.833	1.6		
Methyl iodide		2.2146	.390	1.4		
p-Cymene	66.3	0.7248	.414	1.5		

Summary

The dielectric constants of 35 organic liquids have been determined at the boiling point under a pressure of 760 mm.

A method has been suggested for evaluating the volume occupied by the molecules in the liquid state.

The above idea was applied to Bakker's equation for the latent heat of vaporization.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

THE IONIZATION OF SALT VAPORS

By Wendell M. Latimer Received July 11, 1923

A study of the energies of formation of the simpler chemical compounds seems to offer a promising method of investigating the problems of molecular structure; and now that data are available for the calculation of the heats of ionization of the vapors of the hydrogen and alkali halides, it is important to consider these heats from the standpoints of both the static and dynamic theories of atomic structure. The heats of ionization are also interesting in that they enable us to calculate the degree of ionization of these salt vapors and thus dispel any doubt as to their very slight ionization.

The heat of ionization of a salt vapor may be calculated from the heat of formation of the salt vapor from its elements in the state of monatomic vapors, the ionization potential of the metal and the electron affinity of the negative element. The corresponding equations for sodium chloride are:

$$Na + Cl = NaCl$$
 $\Delta H = -5.05 \text{ volt/equiv.}$
 $Na^{+} + E = Na$ $\Delta H = -5.12$
 $Cl^{-} = Cl + E$ $\Delta H = +3.9$
 $Na^{+} + Cl^{-} = NaCl$ $\Delta H = -6.25$

In order to obtain the heat of the first reaction the values tabulated by Wortenberg and Schulz¹ were used for the heat of formation of sodium chloride from metallic sodium and molecular chlorine,—99,000 cal., the heats of sublimation of sodium metal, 30,000 cal., and of sodium chloride, 48,000 cal., and the value of Trautz and Stackel² for the dissociation of the chlorine molecule into atomic chlorine, 71,000 cal. The change of the heat of the reaction with temperature is less than the experimental error in some of the data and has therefore been neglected. The value for the heat of the reaction in calories, namely, 116,500, has been converted to volt equivalents, since the spectroscopic data which we shall use are more commonly expressed in this unit.

The heat³ of the second reaction, 5.12 volts, is known accurately as the energy corresponding to the head of the (1s-mp) series of sodium. The electron affinity of chlorine, according to Franck's⁴ interpretation of the spectra of the halogens, is given by the head of the series converging at 3180. This value, 3.9 volts, is somewhat in doubt; however, it leads to a heat of

- Wortenberg and Schulz, Z. Elektrochem., 27, 568 (1921).
- ² Trautz and Stackel, Z. anorg. Chem., 122, 81 (1922).
- ³ Compare Foote and Mohler, "Origin of Spectra," American Chemical Society Monograph, Chemical Catalog Co., 1922, p. 65.
- ⁴ Franck, Z. Physik, 5, 428 (1921). Steubing, Ann. Physik, 64, 673 (1921). Angerer, Z. Physik, 11, 167 (1922).

ionization of hydrogen chloride (see Table I) which is in agreement with the experimental value of Foote and Mohler.⁵

In a similar manner (1) the heats of formation from their elements as atomic gases, and (2) the heats of ionization of the hydrogen and alkali chlorides, bromides and iodides have been calculated and are given in Table I. The electron affinity of bromine, 2.9, and iodine, 2.6, and the other data for the alkali halides have been taken from the same sources as those for sodium chloride, except the values for the dissociation of molecular bromine, 42,000 cal., and molecular iodine, 35,000 cal., which are approximate values taken from the calculations of Lewis and Randall.⁶ For the heats of formation of hydrogen chloride, bromide and iodide from their elements as diatomic gases the values of Lewis and Randall have again been used: 22,000, 12,000 and 1500, respectively. The dissociation of hydrogen, 3.1 volts, is that given by Olsen and Glockler.⁷

Table I

Heats of Formation from Elements as Monatomic Vapors and Heats of Ionization in Vapor State

		H		A F	ī		A.	Ħ	
	Formation	Ionization]						1
HC1	-4.05	13.6	HBr	-3.0	13.6	HI	-2.4	13.3	
LiCl	6.1	7.6	LiBr	-5.6	8.1	LiI,	-4.4	7.2	
NaCl	-5.05	6.25	NaBr	-4.5	6.7	NaI	-4.0	6.5	
KC1	-5.3	5.7 -	KBr	-4.75	6.15	KI	-4.2	5.9	
RbCl	-5.4	5.7	RbBr	-4.75	6.05	RbI	-4.2	5.8	
CsCl	-5.4	5.4	CsBr	-4.8	5.8	CsI	-4.2	5.5	

It will be observed that for a given halide the heats of ionization are in the same order as the ionization potential of the positive atoms, and that, in general, the work of ionizing a halide from a positive ion is not much greater than that of removing the valence electron. It may also be observed that these compounds do not form, as is often stated, because of the greater affinity of the halide for the electron. Thus, hydrogen and chlorine combine in spite of the fact that it requires 13.54–3.9 or 9.64 volts to take the electron off the hydrogen and put it on the chlorine.

Ionization Constant for Sodium Chloride

The ionization constant for the reaction, NaCl = Na⁺ + Cl⁻, may be calculated from the relation: $-RT \ln K = \Delta H - T\Delta S$. For ΔH , the heat of ionization, we have found 6.25 volts or 144,000 cal. For ΔS , the entropy change of the reaction of 298 °K. and 1 atmosphere, the value 22.4 is obtained using for the entropy of Cl⁻ 36.3, and of Na⁺ 35.1, as given by the Sackur equation⁸ and for the entropy of sodium chloride 49.0, as given

⁵ Ref. 3, p. 186.

⁸ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923.

⁷ Olsen and Glockler, Proc. Nat. Acad. Sci., 9, 122 (1923).

⁸ Compare Lewis, Gibson and Latimer, This Journal, 44, 1008 (1922).

by the approximate equation of Latimer⁹ for the diatomic gases. Taking ΔC_p for the reaction as 2.5 cal./deg., ΔS_{1725} is 26.8 at the boiling point of sodium chloride. Then for the equilibrium constant at the boiling point, $-1725 \times 4.59 \log K = 144,000 - 1725 \times 26.8$, and for K we find 4×10^{-13} . The partial pressure of either of the ions in the vapor at 1725°K. and 1 atmosphere is then 6×10^{-7} atmospheres. In other words, sodium chloride vapor is ionized to about the same extent as liquid water at ordinary temperatures. Indeed, if we calculate in a similar manner the dissociation of sodium chloride vapor into atomic sodium and chlorine, we find this decomposition to be almost a hundred fold greater than the ionization. Using the same method as that employed for sodium chloride, the ionization constant of all the compounds in Table I may be determined. In every case the ionization would be found to be extremely small.

Heats of Ionization and Atomic Structure

The method which Born¹⁰ has used to calculate the energy of the crystal lattice for the alkali halides has been (1) to determine the field of force about an ion, and (2) from the field of force to calculate the energy of combination as due entirely to the change in electrostatic potential of the ions. We wish to consider the validity of this method in connection with the heats of ionization which have been given in Table I.

Spectroscopic data, as interpreted by the Bohr theory, seem at present to offer the only exact method of determining the field of force about an ion. The simplest case is, of course, the hydrogen ion; and here, from the completeness of Bohr's explanation of the hydrogen spectra, we may conclude that the field of force, up to a few tenths of an Ångström unit (10^{-8} cm.), corresponds exactly to the inverse square for a charge equal to, but of the opposite sign to that of the electron.

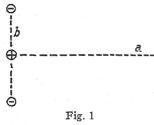
The fields of force for the more complicated ions are not so simple. However, even in these cases, considerable information can be gained from spectroscopic data. Thus, for lithium, the energy of the atom with the electron in the first external, circular orbit may be found from the head of the (2p-ms) series as 3.53 volts. The energy for the corresponding orbit of hydrogen, the 2_2 orbit, is 3.38 volts; and we may calculate from the Bohr theory that the radius of the orbit is 2.08 Å., and at that distance, the field about the lithium ion corresponds to an effective positive charge of 1.02. For the energy levels at greater distances the effective charge approaches unity very closely. For the interval between 2.08 Å. and the inner electrons, the field of force cannot as yet be determined. However, in order to get an approximate value for this field, we may calculate an average position of the two inner electrons in respect to the nucleus

⁹ Latimer, This Journal, 43, 818 (1921).

¹⁰ Born, Verb. Physik. Fes., 21, 13 (1919); 21, 679 (1919).

of 3 positive, Fig. 1, that would give an effective charge of 1.02 at a distance of 2.08 Å., along $a: 3-2 \times \frac{2.08^3}{(2.08^2+b^2)^{3/2}} = 1.02$. This gives b equal to 0.17 Å. Without attempting to attach more than a qualitative significance to the result, the curve for lithium in Fig. 2 has been drawn for the change in the effective charge as the ion is approached along the line "a." Actually, the effective charge must increase somewhat more rapidly than indicated by this approximate treatment.

Likewise, for sodium, we may calculate the energy of the electron in the first external energy level, the 3_8 orbit. In this case it is given by the head of the series at 12,274, and the energy is 1.515 volts. This value corresponds to a radius of 4.8 Å. and an effective charge on the kernel of 1.005 at that distance. If the electrons in the outer shell of the sodium ion were located in definite fixed positions, this value just obtained would serve as a very useful starting point to determine exactly the field at closer distances. At present, although we are confident that the field becomes



more positive closer to the ion, we are not in a position to determine it exactly.

Spectroscopic data are available for similar calculations for all of the alkali metals. However, in the heavier atoms, the first external orbit is out so far, as was the case for sodium, that the field is practically unity, and we are unable to judge the nature of the field closer to

the atom. As yet the spectra of the halides have not been worked out sufficiently to give any definite knowledge in regard to the fields of force about the negative ions. However, we may safely say that at a distance, a chloride ion, for example, acts as a unit negative charge, and at closer distances the sign of the field changes to positive.

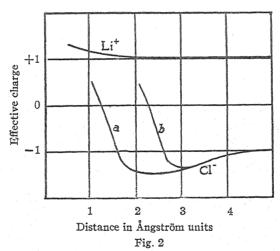
Now let us consider the problem of determining the heats of ionization from the fields about the ions. From our knowledge in regard to the quan-

We may also make use of the assumption that the orbits of the two inner electrons are the same as in helium, in order to obtain an idea of their size. The ionization potential of the first electron of He is 24.5 volts and of the second 54.1. Hence, we may write $78.6 = 2 \times 13.54$ ($2-\alpha$). This gives for α , the screening constant, 0.296. Using this same screening constant for lithium ion, the radius of the orbit would be $\frac{0.53}{3-0.296}$ or 0.2Å. if the orbits were circular. Hence, it would seem that the value obtained for b above is reasonable. It is also interesting to note that if we use this same screening constant for hydride ion we obtain 0.14 volts as the electron affinity of hydrogen. This is about the value to be expected from the stability of the hydride ion.

¹² Birge and Brackett, paper read before the American Physical Society, April, 1923. The relation which these authors have traced between the external and internal orbits seems to give quite accurately the field of force acting upon the electrons of the atomic kernel. It does not, however, give the force acting upon an additional electron.

tum relations in the dynamic atomic systems, it might be predicted that the total decrease in potential energy of the system would be divided equally between the increase of kinetic energy of the electrons and the energy liberated. In such a case it would be meaningless to calculate the heats of ionization in terms of the effective charges on the ions. It is of interest, however, to overlook such an a priori assumption and see how far we can go toward calculating the heat of ionization from the fields of force and the assumption that the energy is due to the change in electrostatic potential of the ions.

In the gaseous molecule of hydrogen chloride the atomic centers are separated 1.27 Å., as determined from the band spectrà¹³ of the molecule. If unit positive and negative charges separated by infinity were brought up to this distance, the decrease in potential energy, eE/d would be 11.3



volts. Experimentally, we have found 13.6 volts for the ionization of hydrogen chloride. This larger value might be accounted for by assuming an increase in the effective charge of the chloride corresponding to Curve a, Fig. 2. However, from a consideration of the heat of ionization of lithium chloride, we obtain quite a different effective charge for the chloride. The closest approach of a lithium ion and chloride ion in the solid is 2.55 Å. The band spectra for the lithium chloride are not known but, in general, the diameters of gaseous molecules are approximately 10% less than in the solid. Using 2.3 Å. as the separation of atomic centers, in order to obtain a change of potential energy of 7.3 volts, we should have to assume that the curve for the effective charge on the chloride ion corresponds roughly to b, Fig. 2.

¹³ (a) Reiche, Ann. Physik, 58, 657 (1919). (b) Urey, This Journal, 45, 1445 (1923).

In other words, the presence of a positive ion affects the whole structure of the chloride ion. It is obvious, then, that the total energy change cannot be found from the change in potential energy of the ions as a whole considered as rigid structures, but must take into account the changes of potential (and probable kinetic) energy of the electrons in each ion as well.

The approximate treatment of the electrons in a dynamic atom, as located in definite positions, may be justified on the ground that these positions represent time average or effective positions. The greatest objection, however, to the treatment of Born and his associates is the assumption of a rigid structure and thus a complete neglect of changes in energy due to the distortion of the electronic arrangement. It would seem that further attempts in this direction are not likely to be profitable.

Summary

A tabulation has been made of the heats of ionization in the gaseous state of the hydrogen and alkali chlorides, bromides and iodides.

The ionization constant of sodium chloride at its boiling point has been found to be 4×10^{-13} .

From a consideration of the fields of force about the ions and the molecular diameters it would seem that the heats of ionization cannot be calculated by any method which treats the ions as rigid structures of electrons about a positive center.

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[Contribution from the Havemeyer Chemical Laboratory, New York University]

A THEORY OF CHEMICAL REACTIVITY

By F. O. RICE

RECEIVED AUGUST 3, 1923

The influence of temperature on the rate of chemical change is so marked that it is obviously a very important factor in any theory of chemical reactivity. Explanations for the high temperature coefficients of chemical reactions usually center round the empirical equation of Arrhenius¹ connecting velocity of reaction and temperature, which in the integrated form is $2.3026 \log k_1/k_2 = \frac{Q}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$. Considering the hydrolysis of cane sugar by hydrochloric acid in aqueous solution, Arrhenius suggested that the cane sugar was present in two forms, active and inactive, in mass-action equi-

¹⁴ Thus, the fundamental idea of G. N. Lewis' theory of valence, that in non-polar compounds a chemical bond consists of a pair of electrons, remains essentially the same whether we consider the electrons as actually located between the atoms or rotating in orbits with that position as their effective location.

¹ Arrhenius, Z. physik. Chem., 4, 226 (1889).

librium, the equilibrium concentration of the active form being very small. In such a case as this it is evident that the concentration of the active form will vary rapidly with the temperature, for it will be proportional to the equilibrium constant of the reaction, active \longrightarrow inactive molecules, and the quantity $\mathcal Q$ in the Arrhenius equation will be the heat of the reaction, active \longrightarrow inactive molecules. The radiation theory offers a similar explanation, except that the two forms of the sugar molecules are not in mass-action equilibrium, the difference between the two forms being due to absorption by the sugar molecule of infra-red radiation, the molecule becoming active when its total energy exceeds a certain value.

It should be noted, however, that there is no a priori reason for supposing that the cane sugar exists in two forms; we might select any one of the three entities, cane sugar, water and hydrogen ion, taking part in the reaction. and by saving that it was present in two forms, we could deduce the Arrhenius equation. The justification for the particular selection would of course depend on the further development of the theory. The criticisms which were made during a recent discussion of the radiation theory,2 and the inability of the theory to explain certain results recently obtained in this Laboratory³ have led me to propose a modification of the Arrhenius theory in which the hydrogen ion is supposed to exist in two forms, active and inactive, in mass-action equilibrium. The active form is identified as the unhydrated hydrogen ion, the hydrated form and the undissociated acid having no catalytic activity; similar assumptions are made for hydroxyl-ion catalysis. Whereas on both the Arrhenius theory and the radiation theory every chemical reaction should have a unique temperature coefficient depending on the heat of activation of the substance undergoing change, it is evident that this new theory predicts that chemical reactions will fall into comparatively few classes, each having a characteristic temperature coefficient. That there is this tendency may be seen from the temperature coefficients obtained in the acid hydrolysis of substances containing the carbonyl group. A very great number of studies of this type of reaction have been made, and almost without exception the value of k_{35}/k_{25} lies between 2.2 and 2.5. The value of k_{35}/k_{25} for the acid hydrolysis of ethyl acetate,4 formyl acetic acid5 and ethyl cyano-acetate6 are all 2.4, within experimental error; on the old theories we have to assume that these compounds all have the same heat of activation or critical increment.

Perhaps the most striking deduction which may be made from this new theory is that stoichiometrically neutral water may not be neutral cata-

² Trans. Faraday Soc., 17, 546 (1922).

³ Rice and Kilpatrick, This Journal, 45, 1401 (1923). Rice and Lemkin, *ibid.*, 45, 1896 (1923).

⁴ Taylor, THIS JOURNAL, 37, 551 (1915).

⁵ Senter and Ward, J. Chem. Soc., 101, 2534 (1912).

⁶ Dushrel, Am. J. Sci., 33, 27 (1912).

lytically. We consider water to be neutral when the total hydrogenand hydroxyl-ion concentrations are equal, and since the unhydrated ions are present in very minute concentrations we shall also have the concentrations of the hydrated ions equal at this point. The concentrations of the unhydrated ions will not be equal, however, and if, as I shall show later, the affinity of the hydrogen ion for water is greater than the affinity of the hydroxyl ion, a stoichiometrically neutral solution will be alkaline catalytically. It is only by making the solution acid stoichiometrically that the concentrations of the two unhydrated ions will become equal and the solution will have a minimum catalytic activity.

Theoretical Outline

Since the views herein expressed are somewhat at variance with those currently accepted I will state briefly the assumptions made in the development of the theory. It is assumed that the law of mass action first enunciated by Guldberg and Waage is correct in its classical form, namely, that the concentration of a substance is a sufficiently exact and complete mode of representing its chemical reactivity. Such statements as "One and the same substance exhibits a different degree of reactivity according to the nature of its surroundings, that is, according to the nature of the medium in which it is dissolved," are explicitly denied. It is not the massaction law but our system of stoichiometric equations that has broken down. For example, it will be shown that if we assume that only the unhydrated hydrogen ion is catalytically active we obtain a satisfactory explanation of experimental results, yet in our stoichiometric equations and in our methods of determining hydrogen-ion concentrations it is implicitly assumed that the total hydrogen ion is catalytically active. It is not surprising, therefore, that the mass-action law fails to hold.

That our stoichiometric equations do not truthfully represent what occurs may easily be seen by considering such reactions as that between the thiosulfate ion and iodine, or between silver nitrate and sodium chloride; even if the reacting species are present in concentrations as low as $0.00001\,N$ the reaction proceeds practically instantaneously, and a great many other cases may be mentioned in which there is practically instantaneous reaction, although the concentrations of the reactants may be very low. It follows, therefore, that even at concentrations as low as $0.00001\,N$ the number of molecular collisions is sufficient to permit a reaction to be practically instantaneous. If, however, we consider reactions which proceed with measurable velocity, the stoichiometric concentrations of the reactants may all be $0.1\,N$ or even higher, yet it may take over an hour for $^1/_{10}$ of the reactants to disappear. The theory explains this difficulty by postulating that in such cases the reactants are not those represented by the stoichiometric equations, but that due to combinations with the

solvent at least one of the reactants is present in very minute concentration with consequent reduction in the number of molecular collisions. On the other hand the radiation theory explains the difficulty by assuming that only a small fraction of the collisions are effective. It may be pointed out here that the rule that the temperature coefficient of a strongly catalyzed reaction should be less than that of a feebly catalyzed one depends upon the possibility of changing a large proportion of inactive to active molecules, in other words of bringing the concentration of the active molecules to ordinary stoichiometric concentrations. In this case the reaction should be practically instantaneous, so that we must conclude on the basis of both the Arrhenius theory and the radiation theory that the temperature coefficient is independent of the velocity of the reaction in those cases in which the velocity is measurable.

I will now consider a particular class of reactions, namely, the case where we have hydrogen-ion catalysis by a strong acid in which the solvent does not enter directly into the reaction. Assuming that the strong acid is practically entirely dissociated, the total hydrogen ion will be present as hydrated hydrogen ion and a minute quantity as unhydrated hydrogen ion; in this case the unhydrated hydrogen ion is supposed to be the only active molecule, so that all these reactions should have the same temperature coefficient. This would hold for any solution in which the hydrogen ion is combined only with water, for the variation with temperature of the concentration of the unhydrated ion depends on its heat of combination. Therefore the temperature coefficient should not be affected by the presence of non-electrolytes or neutral salts, since the affinity of hydrogen ion for water is so great9 that it is unlikely that there will be any extensive combination between the hydrogen ion and these substances. For this conclusion regarding the temperature coefficient to be true, it is necessary to assume that the mass-action law holds and that viscosity effects are negligible. A study of the reaction between acetone and iodine showed that the value of k_{35}/k_{25} was 3.0814 \pm 0.20% whenever the catalyst was a strong acid, although in some cases neutral salts in concentrations from 1 to 4 N, and non-electrolytes in concentrations from 5 to 30% were present. This result is very striking because we were unable to alter the tem-

⁷ W. C. M. Lewis [Scientia, 25, 450 (1919)]. "The fact, that many reactions occur with a finite and measurable velocity, shows us that all the molecules are not in the same chemical state. If they were, the speed of the reaction would either be zero or infinite." Taylor [J. Phys. Chem., 27, 322 (1923)] has put forward a theory of negative catalysis based on these considerations. "The theory emphasizes anew the fact that the concentration of a substance is not the active mass of the substance, but a very much greater quantity."

⁸ Lamble and Lewis, J. Chem. Soc., (a) 105, 2330 (1914); (b) 107, 233 (1915).

⁹ Born, Ber. physik. Ges., 21, 679 (1919). Fajans, ibid., 21, 649 (1919). A résumé of this work is given by Taylor, Newer Aspects of Ionization Problems, Trans. Am. Electrochem. Soc., 43, preprint (1923).

perature coefficient in the slightest degree when the catalyst was a strong acid. When, however, weaker acids were used as catalysts, that is, when the state of combination of the hydrogen ion was affected, the temperature coefficient fell. It will be shown in a later section that with weaker acids the concentration of the hydrated hydrogen ion diminishes with rise in temperature thus giving a lower temperature coefficient.

In reactions which are hydrolytic in character I assume that a compound is formed between the substance A undergoing hydrolysis and the water; that in general only a small fraction of the substance A is present as hydrate, and that the hydrolysis takes place by collision of the unhydrated hydrogen ion with the hydrate. It will be seen that the hydrate of the substance A now becomes an active molecule and the temperature coefficient of the reaction will depend on whether the heat of hydration of A is positive or negative. I have thus covered practically all cases of hydrogen-ion catalysis, and the treatment of hydroxyl-ion catalysis is exactly similar.

We can conclude, therefore, that chemical reactions will fall into comparatively few classes, each class having a characteristic temperature coefficient. The temperature coefficient of a reaction is fixed by the number and nature of the active molecules, and all types of reaction which have the same active molecules will have exactly the same temperature coefficient. The variation with temperature of the concentration of the active molecule will depend on its heat of combination with the solvent or other constituents of the solution with which it combines. According as its heat of formation is positive or negative the concentration of the active molecule will decrease or increase with rise of temperature; an active molecule, therefore, on this theory has no particular virtue because of its internal energy content. If we measure the velocity of a reaction at two temperatures, and substitute the values in the Arrhenius formula we shall obtain directly the heat of combination of the active molecule if its formation is represented by an equation such as $B + C \Longrightarrow A$ where A is the active molecule. In other cases the calculated value of Q will usually be a simple multiple or sub-multiple of the heat of reaction, and in cases where there is more than one active molecule the value of Q will be the algebraic sum of these quantities. Since Q is a heat of reaction, it will vary slightly with the temperature, and this variation could be calculated if the specific heats of the reactants and resultants were known as functions of the temperature. In those reactions which have the same active molecules, the value of Q and its variation with the temperature will be the same.

In concluding this section I wish to refer briefly to unimolecular chemical changes. Perrin² in support of the radiation theory, has pointed out that in unimolecular chemical reactions the velocity is independent of the number of collisions per second and can, therefore, be due only to some out-

side agency, presumably radiation. This argument would be much more convincing if we had an example of a chemical reaction which proceeded with measurable speed and was really unimolecular; all the examples quoted¹0 by Perrin are really pseudo-unimolecular, in which catalysts or traces of water vapor are required for the reaction to proceed. There does not appear to be a single case of a chemical reaction which proceeds with measurable speed and which we are reasonably certain is a true unimolecular reaction. It may be pointed out here that the decomposition of nitrogen pentoxide¹¹ which appeared to be a case of a unimolecular change has now been shown¹² to be at least bimolecular, small traces of the decomposition products being necessary to secure a constant specific rate of decomposition.

Hydrogen-Ion Catalysis by Strong Acids

That there exists in aqueous solution more than one type of hydrogen ion has long been recognized. In a recent paper¹³ Kendall states "the hypothesis of the catalytic activity of the undissociated molecule which purports to explain why the speed of reactions such as ester catalysis is not exactly proportional to hydrogen-ion concentration may be discarded in favor of a view which recognizes several types of hydrogen ion (e. g., H+, [H(H₂O)]+, [H(R.COOR)]+) each possessing a different catalytic activity." The view which I have adopted in this paper is that only the free hydrogen ions are catalytically active, and that these correspond with the active molecules of Arrhenius. When the hydrogen ion is in combination, either as the undissociated molecule or as hydrated hydrogen ion, the resulting compound has no catalytic activity, or a relatively small catalytic activity; these compounds would correspond to the inactive molecules of Arrhenius.

Lapworth¹⁴ and his co-workers first put forward the view that the unhydrated hydrogen ion was the catalytically active particle and that the hydrated hydrogen ion had little or no catalytic activity. They examined a number of widely different cases of hydrogen-ion catalysis in alcohol and showed that all occurred enormously faster in alcohol than in water, and further that the addition of minute quantities of water caused a marked retardation of the velocity. He states, "The proposition that free hydrogen ions are responsible for the catalytic activity of acids leads to the conclusion that they must be relatively few in number in aqueous solution. On the other hand the original conception of hydrogen ions was applied

- 10 Lowry, Trans. Faraday Soc., 17, 596 (1922).
- 11 Daniels and Johnston, This Journal, 43, 53 (1921).
- ¹² Daniels, Wulf and Karrer, *ibid.*, **44**, 2402 (1922).
- 13 Kendall, Proc. Nat. Acad. Sci., 7, 56 (1921).
- ¹⁴ Fitzgerald and Lapworth, J. Chem. Soc., 93, 2163 (1908). Lapworth, ibid., 93, 2187 (1908).

to explain the conductivity of acids in aqueous solution, so that the terms are not synonymous. In the latter case, they must be complex ions, probably of the form (H₂O.H)+." Dawson, 15 from experiments on the reaction CH₃COCH₃ + I₂ in water and water-alcohol mixtures, also supported this view. He showed that in alcohol solutions containing small quantities of water the reaction velocity was proportional to the concentration of the acetone, but was not proportional to the concentration of the acid catalyst. In such solutions the velocity increased much more rapidly than the concentration of acid catalyst. He concludes, "By comparison of the observations in aqueous with those in alcoholic solution we are led to the conclusion that the ionic component responsible for the catalytic effect is the free hydrogen ion, and that the effect of the hydrated ion is relatively unimportant. The concentration of the free hydrogen ions is very small in comparison with the total ion concentration, and in order to produce the observed effects it must be assumed that their specific catalytic activity is Since the ratio of the free hydrogen ion to the total hydrogenion concentration is so small the electrical conductivity of the solution is mainly determined by the complex ions, and the catalytically active ions are of little consequence in so far as the conductivity of the acid solution is concerned."

I will first apply this theory to the case of hydrochloric acid in aqueous solution, since the reasoning applies equally well to all strong acids. Writing the equilibria involved, 16 we have

$$HCl + nH_2O \Longrightarrow HCl.nH_2O$$
 (1)

$$HCl.nH2O \Longrightarrow (H.aH2O) + + (Cl.bH2O) -$$
 (2)

$$(H.aH2O) + \Longrightarrow H^{+} + aH2O$$
 (3)

where n=a+b. The problem is to find out how the unhydrated hydrogen ion in Equation 3 varies with the temperature, for this variation determines the temperature coefficient of the reaction. In the first place I will assume that at temperatures of 0° to 35° Reactions 1 and 2 go practically to completion, that is, that in aqueous $0.1\ N$ solution hydrochloric acid is almost entirely dissociated. The concentration of the hydrated hydrogen ion will not vary, therefore, very much with the temperature, and for small temperature intervals we may write it as a constant without making much error. Considering Reaction 3 at 25° and 35° we have the ratio

of the equilibrium constants $K_{25}/K_{25} = \frac{(\mathrm{H}^+)_{35} \times (\mathrm{H}_2\mathrm{O})_{25}^a}{(\mathrm{H}^+)_{25} \times (\mathrm{H}_2\mathrm{O})_{25}^a}$ and since the heat

of hydration¹⁷ per g. of hydrogen ion is 262,000 cal., this ratio is of the order of 10.¹⁴ Increase in temperature, therefore, strongly favors the formation of the unhydrated hydrogen ion, but unfortunately since we do not know

¹⁵ Dawson, J. Chem. Soc., 99, 1 (1911). Dawson and Powis, ibid., 105, 1093 (1914).

¹⁶ See Kendall and Gross, This Journal, 43, 1416 (1921).

¹⁷ Fajans, Ber. phys. Ges., 21, 709 (1919).

the concentration of the simple water molecules present in the solution nor the number of water molecules in combination with the hydrated hydrogen ion we cannot calculate the change in concentration of the unhydrated hydrogen ion with temperature, which would give us the temperature coefficient of a reaction catalyzed by this acid. We can state, however, that a reaction will have the same temperature coefficient provided it is catalyzed by a strong acid, for the temperature coefficient is fixed by Reaction 3 and this is independent of the kind of acid used provided it is almost entirely ionized. A search of the literature showed that very few such measurements have been made, the great bulk of the studies having been made on reactions which are hydrolytic in character. Harned and Seltz¹⁸ have measured the temperature coefficient of the change, acetyl-chloro-amino-benzene -> p-chloro-acetanilide, catalyzed by hydrochloric acid. Their results give the mean value of k_{35}/k_{25} as 3.14, which is in fairly good agreement with the theoretical value, 3.0814. Slator¹⁹ has studied the temperature coefficients of the reactions between a great number of alkyl halides and sodium thiosulfate. The temperature coefficients in all cases had the value 3 within experimental error, which suggests that these reactions are really cases of hydrogen-ion catalysis. A more rigid test of the theory is at present being conducted in this Laboratory, by measuring the temperature coefficients of the reactions of iodine with various ketones and aldehydes. Mr. C. F. Fryling, using the improved technique³ already described, has found that although the velocities vary widely, all of the temperature coefficients k_{35}/k_{25} have the value $3.081 \pm 0.16\%$, without a single exception. A description of this research will be communicated shortly. Work is also in progress to extend these measurements to other reactions.

Hydrogen-Ion Catalysis by Moderately Strong and Weak Acids

If we write Equations 1 and 2 of the previous section as one equation and generalize by writing X for the acid radical we have: $HX + nH_2O \rightleftharpoons (H.aH_2O)^+ + (X.bH_2O)^-$. In general, this reaction will be exothermic, so that a rise in temperature will send the reaction towards the left. In the case of strong acids where the concentration of the undissociated acid (HX) is very small, an increase of temperature will not affect the concentration of the hydrogen ion $(H.aH_2O)^+$ appreciably, because only a slight movement of the equilibrium towards the left is necessary to alter markedly the value of the equilibrium constant. In the case of weaker acids where the undissociated molecule is present in appreciable amounts, increase in temperature should cause an appreciable diminution in the concentration of the hydrated hydrogen ion $(H.aH_2O)^+$, and this diminution should be

¹⁸ Harned and Seltz, This Journal, 44, 1475 (1922).

¹⁹ Slator, J. Chem. Soc., 85, 1286 (1904).

greater the weaker the acid. The presence of neutral salts might be expected to increase this effect, since their effect is to make the acid appear weaker. It is evident, therefore, that in the case of weaker acids, since the concentration of the hydrated hydrogen ion diminishes with rise in temperature, the increase in concentration with temperature of the unhydrated hydrogen ion is partly neutralized; this means that weaker acids should have lower temperature coefficients than strong acids, a result which is in accord with experiment. The values of Q for the reaction between acetone and iodine when catalyzed by 0.1 N hydrochloric acid and 0.1 N sulfuric acid are 20,540 and 19,070, respectively, so that the ratio $Q(HCI)/Q(H_2SO_4) = 1.077$; this same ratio should be found for any other reaction whatsoever, provided that it is carried on in moderately dilute aqueous solution.

Hydrogen-Ion Catalysis. Hydrolysis

Consider the hydrolysis of ethyl acetate by hydrochloric acid. Writing the equilibrium for ethyl acetate and water we have: CH3COOC2H5 $+ nH_2O \rightleftharpoons CH_3COOC_2H_5, nH_2O$. I will assume that only a small fraction of the ethyl acetate is present as hydrate and that the hydrolysis takes place by collision of the unhydrated hydrogen ion with the ethyl acetate hydrate. If the bulk of the ethyl acetate were present as hydrate or if the heat of hydration of the ethyl acetate were zero we should have a case similar to that treated in the section previous to the last, and the temperature coefficient, k_{35}/k_{25} , would be 3.08. Since, however, we have assumed that the ethyl acetate hydrate is present only in small concentration compared with the total ethyl acetate, the temperature coefficient will be lowered if the hydrate is formed with evolution of heat, and raised if the hydrate is formed with absorption of heat. The heat of dilution of aqueous methyl acetate is positive, which indicates that the hydrate is formed with evolution of heat and hence its concentration will diminish with rise in temperature. The heat of hydration of all esters containing the carbonyl group will probably have about the same value, so that in all cases of hydrolysis of such esters by strong acids the temperature coefficient should be about the same and be less than 3.08. Inspection of the literature shows that almost without exception the values of k_{35}/k_{25} for such reactions lie between 2.2 and 2.5. If instead of ethyl acetate in the above equation we substitute another substance capable of hydrolysis but having a negative heat of hydration, the concentration of the hydrate will increase with rise in temperature and the temperature coefficient, k_{35}/k_{25} , will be greater than 3.08. The value of k_{35}/k_{25} for the hydrolysis of cane sugar^{8b} is slightly over 4, which indicates that the combination of the cane sugar with the water molecule which takes part in the hydrolysis, is an endothermic reaction. It does not seem possible, however, to test this experimentally at present. The results given in the literature for the acid hydrolysis of amides are so contradictory that it is not possible to test the theory in this case either. From the results of Crocker²⁰ and of Kilpi,²¹ $k_{35}/k_{25} = 3.4$. Peskoff and Meyer²² studied the hydrolysis of six amides; the values of k_{35}/k_{25} which they obtained for the different amides were erratic and varied between 2.52 and 3.29.

Hydroxyl-Ion Catalysis

If we write the equilibria involved when a base (B) is dissolved in water we have,

$$BOH + nH_2O \Longrightarrow BOH.nH_2O$$
 (1a)

$$BOH.nH2O \Longrightarrow (B.aH2O) + + (OH.bH2O) -$$
 (2a)

$$(OH.bH_2O) \rightleftharpoons OH^- + b.H_2O$$
, where $n = a + b$. (3a)

I assume here that only the free hydroxyl ion has any catalytic activity, and that when the hydroxyl ion is combined either with water or in the base, the resulting compound has no catalytic activity. The reasoning to be followed then becomes exactly the same as in hydrogen-ion catalysis; all reactions catalyzed by a strong base where the hydroxyl ion is the only active molecule, will have the same temperature coefficient, reactions catalyzed by weaker bases will have a lower temperature coefficient, and reactions involving the hydrolysis of compounds containing the carbonyl group will have a still lower temperature coefficient. As in the case of hydrogen-ion catalysis hardly any data are available for testing this except for the case of hydrolytic reactions. The value of k_{35}/k_{25} for the reaction between acetone and iodine has been measured in this Laboratory by Mr. M. Bergstein, and found to be 2.52 when the reaction was catalyzed by an alkaline buffer solution. Reicher²³ measured the rate of hydrolysis of ethyl acetate by sodium hydroxide at 24.22° and 35.14°; the value of O calculated from these two results is 10,950, whence $k_{35}/k_{25} = 1.82$.

Wilsdon and Sidgwick, 24 and also Boeseken and Verkade 25 have studied the rate of hydration of acid anhydrides. These reactions are not catalyzed by hydrogen ions but are very strongly catalyzed by hydroxyl ions. It is suggested, therefore, that they are really cases of alkaline hydrolysis similar to the case of nitrocamphor investigated by Lowry, 26 the hydroxyl ion being derived from the glass or from organic alkaline impurities in the acetic anhydride. Wilsdon studied the rate of hydration of acetic, propionic and camphoric anhydrides at 18° and 25°. The average value of k_{25} /

²⁰ Crocker, J. Chem. Soc., 91, 593 (1917).

²¹ Kilpi, Z. physik. Chem., 80, 165 (1912).

²² Peskoff and Meyer, *ibid.*, 82, 129 (1913).

²³ Reicher, Ann., 232, 103 (1886).

²⁴ Wilsdon and Sidgwick, J. Chem. Soc., 103, 1959 (1913). Wilsdon, ibid., 107, 679 (1915).

²⁵ Boeseken and Verkade, Verslag Akad. Wetenschappen Amsterdam, 22, 634 (1914).

²⁸ Lowry, J. Chem. Soc., 93, 107 (1908).

 k_{18} was 1.57, average deviation 3.6%, maximum deviation 5.7%. These deviations are probably within experimental error, yet the rate of hydration of acetic anhydride is almost ten times as great as that of camphoric anhydride. Using this average value, Q=11,100 and k_{35}/k_{25} (calculated) is equal to 1.84 as compared with 1.82 for the alkaline hydrolysis of ethyl acetate. Boeseken and Verkade studied the rate of hydration of propionic, butyric and *iso*butyric anhydrides at 0° and 25° , and obtained similar results.

The temperature coefficient for the hydrolysis of amides by alkalies should be somewhat greater than 2.52 which was obtained for the reaction between acetone and iodine when catalyzed by the hydroxyl ion. Peskoff and Meyer have obtained an average value for k_{35}/k_{25} equal to 2.65 for the alkaline hydrolysis of six amides.

Point of Minimum Catalytic Activity

An aqueous solution is ordinarily considered neutral when the total hydrogen-ion concentration is equal to the total hydroxyl-ion concentration, in which case the hydrated forms of the two ions will be present in practically equal concentrations. It will be readily seen that in such a solution the concentrations of the unhydrated forms of the two ions may be very far from being equal, so that a stoichiometrically neutral solution may not be neutral catalytically. Indeed, from the work of Fajans and of Born⁹ it is clear that the smaller the ion, the greater is its affinity for water: therefore, we should expect the hydrogen ion to have a much greater affinity for water than the hydroxyl ion, and consequently in a stoichiometrically neutral solution where the hydrated forms of the hydrogen ion and hydroxyl ion are present in equal concentrations, the unhydrated hydroxyl ion will be present in much greater concentration than the unhydrated hydrogen ion. By acidifying the solution we should reach a point where the concentrations of the two unhydrated ions are equal, and this would be the point of minimum catalytic activity, assuming that the catalytic activities of the two ions are about equal. The phenomenon was first noticed in this Laboratory in some preliminary work concerned with the measurement of reaction velocity. It was found that the saturated borax-boric acid buffer which was supposed to be neutral, catalyzed the reaction at about the same rate as 0.001 N hydrochloric acid. The acetone was finally converted into iodoform which indicated that the catalyst was hydroxyl ion. The matter was not investigated further at that time, the difficulty being overcome by rapid titration of the iodine. Since then the catalytic activity of buffer solutions on the reaction has been studied in this Laboratory by Mr. M. Bergstein, and the results will be communicated shortly. In all the cases investigated a point of minimum catalytic activity was found to lie about PH 5. This abnormal behavior

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of aqueous solutions near the neutral point has been commented on in two papers. Karlsson²⁷ investigated the effect of hydrogen-ion concentration on the stability of methyl acetate and ethyl acetate. The experiments were made at 75° and 85° in presence of a buffer solution of known hydrogen-ion concentration and the esters showed greatest stability at Sörensen (Рн) values between 4.7 and 5.1. Dawson and Powis²⁸ investigated the autocatalytic reaction, $CH_3COCH_3 + I_2 = CH_3COCH_2I + HI$. "If x represents the concentration of hydrogen iodide which has been set free after time t in an originally 'neutral' aqueous solution containing c molecules of acetone per liter and a relatively small quantity of iodine, then the velocity at this moment should be given by dx/dt = kcx, where k denotes the velocity in a solution containing one molecule of acetone per liter and one molecule of halogen acid per liter." The integrated form of the equation is $\ln x$ = kct + a constant, and by extrapolation of the straight line obtained by plotting $\ln x$ as a function of t, the initial speed of the reaction was found. This corresponded to a hydrogen-ion concentration of PH 4.7.

It would appear, therefore, that in order to attain a minimum rate of reaction in aqueous solution, or maximum stability of compounds which are decomposed catalytically, it is necessary to keep the stoichiometric hydrogen-ion concentration near 10^{-5} . The hypothesis that the unhydrated hydrogen and hydroxyl ions are the catalytically active particles provides a satisfactory explanation of these abnormalities. Stoichiometrically neutral water is distinctly alkaline catalytically and it is only when the stoichiometric concentration of the hydrogen ion approaches $P_{\rm H}$ 5 that the solution has minimum catalytic activity. The explanation of Karlsson that the hydrogen and hydroxyl ions do not have the same activity is probably only partly an explanation of the phenomenon, because on his explanation we have to assume that the hydroxyl ion is several hundred times as active catalytically as the hydrogen ion and that this same ratio holds for many different reactions.

Summary

- 1. An explanation for the high temperature coefficient of chemical reactions is offered in which it is assumed that the mass-action law in its classical form is true, and that its apparent failure is due to using stoichiometric equations which do not represent even approximately the reactions taking place in the solution.
- 2. When the ordinary stoichiometric equations are replaced by equations representing more nearly what occurs, it has been shown that certain molecules are connected with an equilibrium constant in such a way that their concentrations vary rapidly with the temperature. These are re-

²⁷ Karlsson, Z. anorg. Chem., 119, 69 (1921).

²⁸ Dawson and Powis, J. Chem. Soc., 101, 1503 (1912).

ferred to as active molecules, and it is due to these that "slow" reactions have a high temperature coefficient.

- 3. The theory predicts that chemical reactions will fall into comparatively few classes, each class having a characteristic temperature coefficient.
- 4. In this theory the assumption is made that the unhydrated hydrogen and hydroxyl ions are the catalytically active particles, and this leads to the conclusion that stoichiometrically neutral water is distinctly alkaline catalytically, and it is not until the hydrogen-ion concentration has a value about $P\pi$ 5 that the concentrations of the unhydrated ions become equal, and the catalytic activity is at a minimum.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

INVESTIGATIONS ON THE PLATINUM METALS. IV.1 THE DETERMINATION OF IRIDIUM IN PLATINUM ALLOYS BY THE METHOD OF FUSION WITH LEAD2

By Raleigh Gilchrist³ Received August 9, 1923

Introduction

A critical study of the Deville and Stas⁴ method for the determination of iridium in platinum alloys was undertaken at the Bureau of Standards as the first of a series of investigations into the analytical methods for the metals of the platinum group.

The Deville and Stas Method

Deville⁵ found that when platinum alloyed with iridium, rhodium, palladium, iron and copper is dissolved in lead at a high temperature, the lead forms alloys with all of the platinum, rhodium, palladium and copper, and with a very small proportion of the iron. The iridium, ruthenium and iron form a separate alloy containing no lead. Boiling dil. nitric acid removes the bulk of the lead together with the palladium and copper and

- ¹ (a) I. The Preparation of Pure Platinum, by Edward Wichers, This Journal, 43, 1268 (1921). (b) II. Investigations on Platinum Metals at the Bureau of Standards, by Edward Wichers and Louis Jordan, *Trans. Am. Electrochem. Soc.*, 43, 385 (1923). (c) III. The Preparation of Platinum and of Platinum-Rhodium Alloy for Thermocouples, by R. P. Neville, *Trans. Am. Electrochem. Soc.*, 43, 371 (1923).
- ² Published by permission of the Director of the Bureau of Standards of the United States Department of Commerce.
 - ³ Associate Chemist, U. S. Bureau of Standards, Washington, D. C.
- ⁴ Deville and Stas, "Procès-verbaux, Comité International des Poids et Mesures," **1877**, p. 185.
 - ⁵ Ref. 4, p. 162.

a small proportion of the platinum and rhodium. Digestion of the residue with warm, dil. aqua regia leaves insoluble only the alloy of iridium, ruthenium and iron.

The Deville and Stas procedure has been used at the Bureau of Standards for six years but with a few modifications in apparatus and technique.

Details of the Analysis Made the Subject of Investigation

In order to arrive at the optimum conditions for the determination of iridium in platinum alloys a study was made of the following details: magnitude of the error caused by the incomplete separation of iridium; variation of the concentration of nitric acid and of aqua regia used; variation of the proportion of lead to alloy and of the time and temperature of the lead fusion; effect of ruthenium, rhodium, palladium, gold and iron and the effect of ignition in air and of reduction in hydrogen on the weight of crystalline iridium.

Preparation of Alloys for Analysis

The alloys were specially prepared for this investigation from metals of the highest purity. The platinum had been prepared for use in thermocouples and its spectrum showed only a trace of calcium. The iridium had been fused with lead and its spectrum showed the presence of traces of platinum, rhodium, ruthenium, lead and iron that were so small, however, that they could have no appreciable effect on the composition of the alloys. The palladium was free from base metals, while the rhodium sponge may have contained a trace of lead, but both were free from the other platinum metals. The spectrum of the gold indicated a trace of silver and copper.

The alloys were melted in an Ajax-Northrup high frequency induction furnace^{1c} using pure lime or purified thoria as the refractory. The platinum used was either in the form of an ingot or of wire compressed into a pellet in a steel mold. The finely crystalline iridium was wrapped in a small cylindrical shell of pure platinum in order to avoid loss. The molten alloys were stirred vigorously by the effect of the induced electric current. With the exception of the iron-iridium alloy which was cast in graphite the melts were allowed to freeze in the crucibles.

From experience gained in the melting of preliminary samples of pure platinum and of platinum-iridium alloys, the small loss in weight on melting was considered to be a loss of iridium. The percentage of iridium put into the mixture of metals represented, therefore, the maximum iridium percentage of the alloy, while the minimum average percentage was calculated by deducting the percentage loss in weight which occurred in melting.

Danger of Non-Uniform Sampling

Early analyses indicated the necessity of careful sampling because of the non-homogeneity of some of the alloys. The first alloy of the final series (containing 20% of iridium) was drawn to wire of 0.60mm. diameter and cut into fragments varying from 1 to 2 mm. in length. The variation in analytical results led to the belief that this method of sampling was inadequate. The subsequent alloys made were drawn to 0.36 mm. and cut into lengths of 1 mm. The cut wire in every case was cleaned from superficial iron by hot coned. hydrochloric acid, washed with distilled water and ignited to dull redness in a porcelain crucible. Samples for analysis were taken from different parts of the mass.

Results of Analyses

Incomplete Determination of Iridium.—Early in the experimental work iridium was detected qualitatively in the aqua regia solution. Although the amount in this case was small, it was evident that some iridium was being lost. In order to determine the magnitude of this error, iridium was recovered from the aqua regia solutions in the analysis of a number of the alloys. The total aqua regia solution was evaporated to dryness, the nitric acid eliminated by hydrochloric acid, ammonium chloride added, the mass of salt dried, reduced in hydrogen and the resulting metal fused with lead as in the regular procedure for an alloy. Calculated in percentage on the basis of the weight of the alloy samples taken, of the 33 recoveries made 20 were less than 0.05%, 7 were between 0.05 and 0.10%, 4 were between 0.10 and 0.15%, and 2 were between 0.15 and 0.30%.

There was no uniformity in the quantity of iridium which escaped the first determination, considering either individual experiments or the averages from different alloys, although these alloys differed considerably in iridium content. It seems unlikely that more than a very small quantity could have been involved in a mechanical loss, since the utmost precautions were taken to effect a quantitative transfer and a double filter was used, both layers of which were of paper of close texture. There was probably some solution of the iridium by the aqua regia in all cases, but the reason why the amount dissolved should vary between wide limits is not apparent. In reporting the analyses in which this second determination of iridium was made, the total iridium is the value considered in the discussion of the results. Such recoveries were made except in the analyses discussed under the headings "Variation of the Concentration of Nitric Acid," "Effect of Palladium and Gold" and the "Effect of Iron."

Experiments on the Variation of the Concentration of Nitric Acid Used to Disintegrate the Lead Button.—Eight analyses were made on 4g. samples of an alloy containing a maximum of 4.85% of iridium and a minimum of 4.82%. Each of the three analyses in which the nitric acid concentration was 1:8 gave the value 4.83%. Three determinations with 1:4 nitric acid gave 4.83, 4.85 and 4.83%. Two determinations with 1:2 nitric acid gave 4.79 and 4.80%.

Although the variation of the concentration of nitric acid had little effect on the iridium determination, it was found that the 1:2 nitric acid produced a residue which was finely divided and difficult to filter, thereby offsetting any advantage gained over the 1:4 nitric acid by a saving of time.

In this and subsequent experiments the temperature of the solutions was maintained at about 85° (steam-bath) and double filters were always used.

Experiments on the Variation of the Concentration of Aqua Regia Used to Separate the Iridium from the Lead-Platinum Alloy.—Seven analyses were made on 2g. samples of an alloy containing a maximum of 20.20% of iridium and a minimum of 20.11%. The average of three experiments, with 1:10 aqua regia was 19.99%; that of two experiments with 1:5 aqua regia, was 20.09%; and that of two experiments using 1:2.5 aqua regia was 20.06%. The seven individual results varied from 19.98 to 20.12%.

Such variations as appear in the results are probably to be ascribed to somewhat inadequate sampling rather than to the variation of the concentration of the aqua regia. Consistent results were obtained in the analysis of a 10% iridium alloy and of a 5% iridium alloy containing gold and palladium, in which analyses the concentration of aqua regia was 1:2.5.

Experiments on the Variation of the Duration of the Lead Fusion.— Nine analyses were made on 2g. samples of an alloy containing a maximum of 20.20% of iridium and a minimum of 20.11%. The average of three experiments with a 4-hour fusion period at 1000° was 19.99%, of two with a 2-hour period was 20.05%, of two with a 1-hour period was 20.11%, and of two with a 1/2-hour period was 20.05%. The nine individual results varied from 19.98 to 20.12%.

The results show that the time of fusion with the temperature at 1000° may vary over a wide range without affecting the determination.

Experiments on the Variation of the Proportion of Lead to Alloy.—Seven analyses were made on 2g. samples of an alloy containing a maximum of 20.20% of iridium and a minimum of 20.11%. The average of two experiments, with 10 g. of lead to 1 g. of alloy, was 20.05%, of three, with 20 parts of lead, was 19.99% and of two, with 40 parts of lead, was 20.02%. The seven individual results varied from 19.97 to 20.09%. The proportion of lead can, therefore, be varied over a wide range without appreciably affecting the determination.

Experiments on the Variation of the Temperature of the Lead Fusion.— Analyses were made of an alloy containing a maximum of 10.26% of iridium and a minimum of 10.22%. Experiments in which 10 parts of lead to 1 part of alloy at 600° were used resulted unsatisfactorily. It was not possible to effect complete fusion. Two analyses on 1.3g. samples with a lead fusion at 800° for 1/2 hour gave 10.26 and 10.34%. Two analyses on 1.3g. samples at 800° for 4 hours gave 10.18 and 10.13%. Three

analyses on 4g. samples at 1000° for 1/2 hour each gave 10.22%. Three analyses on 4g. samples at 1000° for 4 hours gave 10.18, 10.18, and 10.12%. The results show that the temperature of the lead fusion may vary between 800° and 1000° without seriously affecting the determination. However it appears that a short fusion at 800° is not sufficient.

Experiments to Determine the Effect of Ruthenium.—Three analyses were made of an alloy containing a maximum of 9.96% of iridium and 0.51% of ruthenium and a minimum of 10.35% of iridium plus ruthenium. One experiment on a 4g. sample gave 10.44% and two experiments on 3.5g. samples gave 10.39 and 10.41%. The results confirmed the observation of Deville and Stas⁶ that ruthenium separates quantitatively with the iridium.

Experiments to Determine the Effect of Rhodium.—Five analyses were made of an alloy containing a maximum of 5.06% of iridium and a minimum of 5.01% and in addition 5.04% of rhodium. Three analyses on 4g. samples gave 5.14, 5.15, and 5.18%. Two analyses on 3.4g. samples gave 5.13 and 5.17%. The results of the two series of analyses, although concordant, are higher than the maximum percentage of iridium in the alloy. The iridium from two experiments was examined chemically for rhodium, but in both cases a quantity of rhodium not greater than 0.01% of the weight of the alloy sample taken for analysis was extracted. Iridium from a third experiment was examined by spectrographic analysis but the quantity of rhodium detected was very small. It was, therefore, concluded that the actual experimental values for iridium represented the true composition of the portion of the ingot which was prepared for analysis. Deville and Stas⁵ state that rhodium does not interfere in the determination of iridium.

Experiments to Determine the Effect of Palladium and Gold.—Six analyses were made on 4g. samples of an alloy containing a maximum of 5.35% of iridium and a minimum of 5.31% and in addition 3.07% of palladium and 2.32% of gold. Three experiments, with 1:8 nitric acid, gave 5.25, 5.29, and 5.30%. Three experiments, with 1:4 nitric acid, gave 5.29, 5.28, and 5.31%. The results show that palladium and gold have no effect upon the determination of iridium.

Experiments to Determine the Effect of Iron.—Five analyses were made on 4g. samples of an alloy containing a maximum of 4.75% of iridium and in addition 0.31% of iron. The results ranged from 5.03 to 5.12% with an average of 5.07%. The iron in the combined nitric acid and aqua regia solutions from three of these analyses was determined colorimetrically and found to be 0.02, 0.01, and 0.005% of the sample. One of the remaining solutions showed a trace of iron and the other none. Colorimetric analysis of iron in a separate sample of the alloy gave 0.31% of iron.

⁶ Ref. 4, pp. 162, 191.

A procedure for the separation of iron from iridium, suggested by W. H. Swanger of this Laboratory, was tested. It consisted of a fusion of the iridium with zinc, removal of the excess of zinc with hydrochloric acid, and fusion of the zinc-iridium alloy with potassium pyrosulfate. The insoluble residue from the digestion of the pyrosulfate fusion with dil. sulfuric acid should contain all of the iridium free from iron but contaminated with silica. After the removal of silica in the usual manner four experiments gave 4.65, 4.65, 4.71 and 4.72%.

To determine whether this procedure could be conducted without loss of iridium, experiments were made with samples of iridium containing no iron. The samples weighed 0.1940 g., 0.1945 g. and 0.1938 g. and the recoveries were 0.1951 g., 0.1933 g. and 0.1937 g., respectively.

The results of the experiments confirm the observation of Deville and Stas⁷ regarding the behavior of iron and show in this case that even a greater proportion of the iron separated with the iridium. In the analysis of some contact points containing approximately 5% of iridium and 0.16% of iron, it was also found that nearly all of the iron was weighed as iridium.

Analysis of an Alloy Containing a Small Amount of Iridium.—Three analyses were made of an alloy calculated to contain 0.084% of iridium. The samples weighed 5 g. and the results were 0.070, 0.068, and 0.066%, with an average of 0.068%. The values are seen to be slightly low. It was in the analysis of this alloy, among the first made in this investigation, that iridium was observed to be present in the aqua regia solution.

Miscellaneous Experiments.—A correction of 0.0005 g., the quantity of insoluble material introduced into the iridium during the analysis from the reagents and apparatus used, was applied to the weight of the iridium in all of the analyses reported in this paper.

It was found experimentally that in the time required for the ignition of the iridium in air in the regular analysis, namely, about one hour, there would be no significant loss in weight.

It was found experimentally that the practice of reducing and cooling the iridium in hydrogen introduced no error into the weight of the iridium.

Spectrographic examination of samples of iridium obtained from analysis showed that platinum and lead were either absent or their presence doubtful. No zinc was found in the iridium which had been fused with zinc and subsequently with potassium pyrosulfate.

Proposed Modified Procedure

The following modification of the Deville and Stas method is recommended.

1. Lead Fusion.—Fuse the carefully sampled platinum alloy with 10 times its weight of granular test lead for a period of one hour at a tem-

⁷ Ref. 4, p. 177.

perature of about 1000°. A covered crucible, whose outside dimensions are 4 cm. in diameter and 7 cm. in height, machined from Acheson graphite, is suitable for fusions made with 20 to 40 g. of lead. The inside of the crucible should possess a slight taper to facilitate the removal of the cooled ingot. Do not pour the fusion from the crucible, but allow it to solidify, since the iridium has largely settled to the bottom of the crucible. The crucible is best heated with an electric furnace.

- 2. Disintegration with Nitric Acid.—Brush the cooled lead ingot free from carbon with a camel's hair brush, and place it in a beaker. Add nitric acid of the concentration one volume of acid (d., 1.42) to 4 volumes of water, using 1 cc. of acid per g. of lead. Place the beaker on the steambath or on a hot-plate which maintains the temperature of the solution at about 85°. Disintegration of the lead ingot is usually complete in about two hours, and leaves a rather voluminous, gravish-black mass. Dilute the solution to twice its volume and decant the liquid through a double filter, consisting of a 9cm. paper of fine texture8 on which is superimposed a 7cm, paper of looser texture. Wash the residue quite thoroughly with hot water and pass the washings through the filters. The residue is not transferred to the filters at this point. The lead nitrate solutions and washings are best caught in an Erlenmeyer flask to make easier the detection of the presence of any residue which has passed through the filters. This is done by whirling the liquid in the flask. Any particles of the residue collect at the center of the bottom of the flask. Return the filters to the beaker without ignition.
- 3. Solution of the Lead-Platinum Alloy by Aqua Regia.—Add in order 15 cc. of water, 5 cc. of hydrochloric acid (d., 1.18) and 0.8 cc. of nitric acid (d., 1.42) for each gram of the platinum-alloy sample taken. Heat the solution in the beaker on the steam-bath or on a hot-plate which maintains the temperature at about 85°. The lead-platinum alloy is usually completely dissolved within one and a half hours. Dilute the solution with twice its volume of water and filter through a double filter, similar to the one used for the lead nitrate solution. The iridium, insoluble in the aqua regia, is in the form of fine crystals, possessing a bright metallic luster and having a high density. Pass the clear solution through the filter first and then transfer the thoroughly macerated paper. It is very important to examine the beaker to see that no iridium remains. To do this the interior of the beaker is wiped with a piece of filter paper to collect any metal adhering to the sides. Then by whirling a small quantity of water in the beaker any iridium remaining gravitates toward one place whence it can be removed with a piece of paper. Wash the filters and iridium thoroughly, first with hot water, then with hot dil. hydrochloric

⁸ Such as S. and S. No. 589 blue ribbon and No. 589 black ribbon papers, respectively.

acid (1:100), and lastly with hot water. The chloroplatinic acid filtrate and washings should be examined for iridium, which may have passed through the filters, in the manner described under the nitric acid treatment. The last washings should be tested for the absence of lead.

4. Ignition and Reduction of the Iridium.—Place the washed filters and iridium in a porcelain crucible and dry, before igniting in air. After the destruction of the filter paper, ignite the iridium strongly with the full heat of a Tirrill burner. After all carbon is burned out, cover the crucible with a Rose lid, preferably of quartz. Introduce into the crucible a stream of hydrogen, burning from the tip of a Rose delivery tube (a quartz tube is preferred). After five minutes remove the burner and a few minutes later extinguish the hydrogen flame by momentarily breaking the current of hydrogen. This is best done by having a section of the rubber delivery tube replaced by a glass tube, one end of which can easily be disconnected. Allow the iridium to cool in an atmosphere of hydrogen and then weigh as metallic iridium.

In commercial analysis no effort is made to correct the weight of iridium for small amounts of ruthenium. Correction, if desired, can be made according to the original directions of Deville and Stas. The correction for iron can be made according to the procedure given with the discussion of the analysis of the iron-iridium-platinum alloy.

Acknowledgments are made to Edward Wichers, under whose supervision the chemical work on the platinum metals was conducted, to R. P. Neville, who melted the alloys and prepared them in the form of wire, and to Florence J. Stimson, who made the spectrographic analyses of the iridium samples.

Summary

A study has been made of the analytical details of the Deville and Stas method for the determination of iridium in platinum alloys containing from 0.1 to 20% of iridium. Specially prepared alloys, made from highly purified metals, were used in the investigation. It was found that the concentration of nitric acid, the concentration of aqua regia, the proportion of lead, and the time and the temperature of the lead fusion can be varied over a wide range without affecting the determination. The observations of Deville and Stas that palladium and rhodium have no effect upon the determination and that ruthenium separates quantitatively with the iridium were confirmed. In addition, gold was found not to interfere. Iron separates nearly quantitatively with the iridium as observed by Deville and Stas. A method for the separation of iron from the iridium was tested and found to give satisfactory results. The loss in weight of crystalline iridium during the ignition periods is insignificant and the weight of crystalline iridium is not affected by heating and cooling in an atmosphere of

hydrogen. Spectrographic examination of samples of iridium from analysis showed that neither platinum nor lead was present in sufficient quantities to affect the determination. The iridium results tend to be low by a variable but usually small amount. One factor in this error is a slight solution of iridium by aqua regia. A modified procedure for the method is offered which combines the optimum conditions for speed and accuracy in the various details of manipulation.

A full report of this investigation including the actual experimental data will be found in a forthcoming publication of the Bureau of Standards.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

SOLUBILITY. IX. METALLIC SOLUTIONS

By J. H. Hildebrand, T. R. Hogness and N. W. Taylor Received August 13, 1923

In a series of papers¹ appearing during the past seven years by the senior author and various collaborators considerable evidence has been presented to show that deviations from Raoult's law, and accompanying effects upon solubilities, can be predicted approximately for substances that are sufficiently non-polar, provided they do not tend to form compounds with each other. These deviations were correlated chiefly with differences in "internal pressure," as estimated by various criteria.

Metallic solutions offer a particularly inviting field for the application of a theory of solubility because a large amount of data is available and also because the metals differ among themselves in surface tension, compressibility, expansion, internal pressure and other characteristics far more than do the familiar non-metallic liquids, so that they offer a much more severe test of a theory than do most non-metallic solutions. For example, although but few non-metallic liquids, excluding water, are sufficiently unlike to yield two liquid phases, there are known no less than 47 metallic pairs which are incompletely miscible in the liquid state.

We do not have data upon the coefficients of compressibility and expansion for molten metals necessary for the calculation of their internal pressure by the expression $T_{\alpha/\beta}$, used in earlier papers, except for mercury, where the value is 13,200 megabars. This is several times as large as the values for the common non-metallic liquids, which explains, at least partly, their immiscibility with mercury. We may, perhaps, form a rough idea of the internal pressures of liquid metals from the values of α/β of their solid forms. Table I gives some figures of this sort taken

¹ Compare particularly This Journal, 38, 1452 (1916); 39, 2301 (1917); 41, 1067 (1919); 42, 2180 (1920); 42, 2213 (1920); 43, 500 (1921); 43, 2172 (1921); 45, 682 (1923). *Phys. Rev.*, 21, 46 (1923).

 $^{^{2}}$ α is coefficient of expansion; β of compressibility.

from a paper by T. W. Richards.³ We may also note that the tensile strengths of the metals are in somewhat the same order, nickel, platinum, iron and copper, for example, having high tensile strengths, lead, sodium, bismuth, etc., low strengths.

Table I

Relative Internal Pressures of Solid Metals Estimated from Expansion and

Compressibility

α	\times 10 6	$\beta \times 10^8$	α/β		$\alpha \times 10^6$	$\beta imes 10^8$	α/β
Nickel	42	43	98	Mercury (liq.)	180	395	46
Silicon	23	32	72	Lead	88	233	38
Platinum	27	38	71	Cadmium	74	210	35
Gold	43	64	67	Tin	67	190	35
Copper	50	75	67	Sodium	220	1560	14
Iron	36	60	60	Bismuth	40	300	12.5
Silver	57	101	56	Potassium	250	3170	7.9
Zinc	87	170	51	Cesium	330?	6100	5.4
Aluminum	72	147	49				

The surface tension of molten metals may be expected to give a truer indication of the internal forces of the liquid than it does in the case of most compounds, because the molecules are simple and symmetrical and little or no orientation should take place in the surface. We may use the expression $\gamma/V^{1/3}$ or, where data are available, $E_{\sigma}/V^{1/3}$, where γ is the surface tension, V the molal volume and E_{σ} the surface energy. We have accurate measurements by Hogness⁴ for the surface tensions of mercury, bismuth, cadmium, lead, tin and zinc. Most values for the other metals are unsatisfactory and conflicting due partly, at least, to failure to prevent

Table II

Relative Internal Pressures of Metals from Surface Tensions

	γ	t°	Εσ	$\gamma/V^{1/2}$	$E\sigma/V^1/s$
Platinum	. 18195	1800			
Iron	. 9505	1600		490	
Silver	. 7825	1000		348	
Copper	. 5815	1100		294	
Gold	6126	1070		282	
Zinc	. 755	450	820	350	380
Cadmium	. 622	450	662	356	274
Mercury	. 393	350	580	157	232
Tin	. 514	450	572	198	222
Lead	. 438	450	494	163	182
Bismuth	. 367	450	413	133	150
Potassium	. 4121	62		114	
Sodium	. 2941	90		92	

³ Richards, This Journal, 37, 1643 (1915).

⁴ Hogness, *ibid.*, **43**, 1621 (1921).

⁵ Quincke, Pogg. Ann., 135, 642 (1868); 138, 141 (1869).

⁶ Heydweiler, Wied. Ann., 62, 694 (1897).

the formation of an oxide film. Table II gives values for a number of the more important metals. On account of the difference in temperature the magnitude of $\gamma/V^{1/a}$ for the first five metals is much less than it would be if all of the metals in the table could be compared at the same temperature; accordingly, we are justified in concluding that their internal pressures would be found higher, at the same temperature, than those of the second group, zinc, bismuth, inclusive. It will be noted that the order is not very different from that given in Table I where, of course, crystal structure introduces disturbing factors.

The only other method applicable to the metals is the one using the heat of vaporization. Table III gives values of L/V, which again show approximately the same order, except that the most volatile, mercury and cadmium, are shifted considerably downwards. Table II, however, seems to be more closely correlated with our present knowledge of intermetallic systems.

TABLE III

RELATIVE INTERNAL PRESSURES OF	METALS FRO	M HEATS	OF VAPO	RIZATION
	L	V	Ĺ	L/V
Nickel	. 69,200	6.71	1450	10,300
Copper	. 66,900	7.56	1083	8,770
Iron	. 70,600	8.11	1530	8,700
Silver	. 61,800	11.3	961	5,500
Aluminum	. 52,500	11.2	658	4,560
Tin	. 66,200	16.9	232	3,920
Zinc	. 28,800	10.1	419	2,850
Lead	. 45,700	20.0	327	2,410
Thallium	. 39,600	17.2	302	2,300
Bismuth	. 42,200	20.8	269	2,030
Cadmium	. 25,000	14.1	321	1,770
Mercury	. 14,400	15.5	300	973

We will now proceed to examine the solubility data to determine how far the arrangement in these tables corresponds to the mutual solubilities of the metals. We must be prepared, of course, to find solubilities greater than internal pressure differences alone may lead us to expect, due to compound formation, even though the attractions between the compounds may be insufficient to cause the separation in the solid state of any recognizable compounds. If the electron theory were more highly developed with reference to liquid metals we would doubtless be more prepared than we now are to predict compound formation and its attendant effects upon solubility. There is great need of enlightenment regarding the nature of intermetallic compounds.⁸

We will first consider the group of metals, zinc, cadmium, mercury, tin, lead, bismuth, which according to Table II have internal pressures

⁷ Hildebrand, THIS JOURNAL, 41, 1067 (1919).

⁸ However, compare Kraus, ibid., 44, 1216 (1922).

decreasing in that order. We have very accurate data by Taylor, on-cerning the activities, a, of these metals in a number of their liquid alloys, obtained by measuring e. m. f.'s of concentration cells. Taylor found that the pairs given below in Table IV give positive deviations from Raoult's law of the normal type. Writing Raoult's law as a = N, where N is the mole fraction, the deviation may be expressed by the value of $\log (a/N)$.

Table IV
Activity Coefficients in Various Alloys

		THE ELECTRICATE AND THE AT	MICOUS ILLIUOIS	
Allov	ŧ	$\Delta(E\sigma/V^{1/3})$		
moy	•	$N_{\rm Cd} = 0.1$	$N_{\rm Cd} = 0.2$	A(250/ V 79)
Cd-Sn	483	0.228	0.185	52
Cd-Pb	480	.455	.369	92
Cd-Zn	466	. 560	.373	106
		Log (a/?	V) for tin-	
		$N_{\rm Sn} = 0.1$	$N_{\mathrm{Sn}} = 0.2$	
Sn-Zn	466	0.460	0.274	158
Sn-Cd	463	.251	.185	52

The values of a/N for the three cadmium alloys are in the same order as the differences between the internal pressures of the components, using $E_{\sigma}/V^{1/s}$ to indicate the latter. It will be seen that the deviations are not, however, strictly proportional to these differences in internal-pressure. The same is true for the two tin alloys. Taylor also obtained results for cadmium-bismuth alloys. We might expect here to find a large deviation on account of their large internal-pressure difference. As a matter of fact, the deviation from Raoult's law is small, but of so irregular a type as to make its non-conformity to the internal-pressure theory not at all strange. The phenomena in this mixture are evidently rather complex.

Freezing point-composition diagrams are available which permit us to give the freezing-point lowering for a given solvent and a series of solutes at a fixed composition which, in the absence of "chemical" effects, should

TABLE V

Sor	LUBILITIES OF BISMU	TH, ZINC AN	d Tin			
Solvent		Bi at 250°	Zn at 375°	Sn at 180°		
Zn		2 liq.10		0.6810		
Cd		$0.905^{13,14}$	0.89610	$0.71^{10,13}$		
Hg		0.920^{11}	0.90411	0.735^{12}		
Sn		0.93310	0.82010			
Pb		0.94814	2 liq.	0.73513		
Bi			2 liq.	0.7610		

⁹ This Journal, 45, 2865 (1923).

¹⁰ Heycock and Neville, J. Chem. Soc., 71, 383 (1897).

¹¹ Puschin, Z. anorg. Chem., 36, 201 (1903).

¹² Van Heteren, ibid., 42, 129 (1904).

¹³ Stoffel, ibid., 53, 137 (1907).

¹⁴ Kapp, Dissertation, Königsberg, 1901.

place the metals in the order of their internal pressures. It is always most striking to consider the series obtained for the substances of highest and lowest internal pressure, for then there is no ambiguity as to the true order as there is when an element in the middle of the series is chosen for comparison, and when deviations do not differentiate the element of higher internal pressure from the one of lower. Table V, accordingly, gives the solubilities of bismuth and zinc in the series of metals falling between them in Table II also those of tin, in the middle of the series, whose

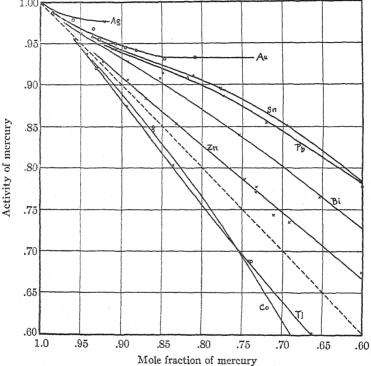


Fig. 1.—Activities of mercury in various amalgams

solubilities should show a maximum in the adjacent members. The figures were obtained from smooth curves drawn through the points given by the observers cited.

It will be seen that the agreement in the case of bismuth is perfect; for zinc it is nearly so, the positions of cadmium and mercury being reversed; for tin the only irregularity is its abnormally great solubility in bismuth, corresponding to the result found by Taylor, previously cited. Similar results are obtained with lead and cadmium.

The deviations of amalgams from ideality are shown by the vapor-pres-

sure measurements by the senior author and his collaborators, 15 summarized in the plot of a against N shown in Fig. 1. We see here more irregularity than in the other cases. With cadmium there is negative deviation, showing that the atoms of these elements attract each other to a greater extent than they attract their own kind. With zinc the deviation is positive but, just as in Table V, less than we might have expected, which may indicate the same sort of effect that is shown more obviously with cadmium, its nearer neighbor in sub-group 2 of the Periodic System. Again bismuth, which is below tin and lead in Table II, shows a smaller deviation than lead and tin. In brief, mercury seems to show more evidence than we have previously seen of greater attractions for certain other elements than internal pressures alone would lead us to expect. Cases of this sort multiply greatly with other systems to be considered in the following paragraphs. It is interesting to note the great deviations with silver and gold, which will be found in harmony with the positions of these metals in a later and more extensive table.

The construction of a more general table of internal pressures of metals is made difficult by the lack of accurate data concerning their physical properties in the liquid state, by the inferior accuracy of much of the solubility data, and by the frequency with which solid solutions and compounds occur, the former making the freezing-point data of less significance for our purpose, and the latter introducing a factor with which the simple internal-pressure theory is incompetent to deal. The table we have attempted to construct is, therefore, somewhat approximate in character and subject to later modification as our knowledge of the field is extended. In its construction we have been guided by what knowledge we possess of the physical properties of the metals, by the freezing-point data in cases where simple eutectics occur, by the existence of two liquid phases in many cases, showing extreme mutual insolubility, by the existence of solid solutions of simple type showing great similarity between the components, and by the Periodic System, which we have assumed to indicate the approximate positions of elements that belong to series already established. We have noted in general that internal pressure decreases from top to bottom of a group. Upon finding, for example, as in Table II, that internal-pressures decrease from zinc to mercury, we feel justified in assuming that the internal pressure of magnesium is higher than that of zinc.

The evidence is so large in volume but so inconclusive in many of its individual items, that it does not seem worth while to attempt to present it in detail beyond what is shown in Table VI, itself. This table lists the

¹⁵ Zinc: Hildebrand, *Trans. Am. Electrochem. Soc.*, **22**, 319 (1923). Silver, gold, bismuth and thallium: Hildebrand and Eastman, This Journal, **36**, 2020 (1914); **38**, 785 (1916). Cadmium, tin and lead: Hildebrand, Foster and Beebe, *ibid.*, **42**, 545 (1920).

Pb

TI

M Bi Na i i

i i i

i

1

cases in which binary alloys show either two liquid phases or solid solutions, and omits the compounds, which introduce complications rather than contradictions to the internal-pressure theory. The data have been derived from the usual sources, beginning with the Landolt-Börnstein "Tabellen."

TABLE VI INTERNAL PRESSURE SERIES FOR LIQUID METALS High ← Internal Pressure → Low Bi Na K Co Ni Al Cu Mg Ag Au Zn Cd Hg Sn Pb TI C High Cr Si i i i Mn i S Fe Co s S S Ni S S i Al Cu S s Mg Ag i Internal I PD Cd Hg s Sn i

^a The letters have the following significance: i, 2 liquid phases; S, complete solubility in the solid state; s, limited solubility in the solid state.

s

i

î

Each space in Table VI corresponds to the mixture of the two metals whose symbols are at the left-hand side and at the top, respectively. The diagonal is drawn through the intersection of each symbol with itself, so that the nearer a space is to this diagonal the closer are the two metals to each other in internal pressure. The portions of the table on the two sides of the diagonal are, of course, essentially identical, but the presence of both will be found convenient. Those combinations which yield two liquid phases are denoted by "i" (insoluble), those which yield a complete series of solid solutions by "S," and those showing limited solubility in the solid state are denoted by "s." Where the system has not been investigated, or where compounds have been found, the space has been left blank, so as not to complicate the table.

We must recall, first of all, that the internal-pressure theory cannot predict tendencies towards the formation of compounds, or abnormally great attractions between the atoms of unlike metals, so that negative deviations from Raoult's law, or even abnormally small positive deviations or, in other words, abnormally great solubilities, are not contradictory to the theory. All that can be expected is that insolubility cannot occur unless

there is sufficient difference in internal pressure, although even then it may not occur if tendency towards compound formation exists. Let us now examine the table with this in mind. It will be seen that there are no i's within a certain distance of the heavy diagonal, denoted by the dotted lines, indicating that there are no cases of insolubility in the liquid state among the metals adjacent to each other. A separation of at least five places is necessary. This may not seem very great, but reference to Table II will show that it corresponds to about 100% difference in internal pressure, almost as great as the entire difference from top to bottom of the table in our third paper 16 for non-metallic liquids. There would undoubtedly be found still more insoluble pairs if it were not for differences in boiling point, as between mercury and iron, which make it difficult or impossible to investigate the system. Even in such cases, however, the table is significant with regard to other phenomena, such as wetting, which likewise requires sufficiently great attractive forces between the two metals concerned. It is well known, for example, that pure mercury will not wet iron.

Turning to the consideration of solubility in the solid phases as an indication of probable likeness in the internal pressures of the liquids, when compounds are not formed, we find that 21 cases of solid solution are found in the spaces between the dotted line and the heavy diagonal, the region in which insolubility in the liquid form is absent, while but 17 cases occur outside this region, although the possible combinations in the other two regions are 57 in the former and 153 in the latter. In other words, solid solutions are known to occur in 37% of the possible combinations among metals within five places of each other in the internal-pressure series, while they are known among but 11% of the possible combinations of metals more than four places removed. If we consider metals removed less than eight places from each other, as compared with those eight or more places removed, giving equal numbers of possibilities in the two groups, we find 42 instances of solid solution among the former group and only 6 among the latter.

Table VI will be found useful, therefore, in predicting and correlating (a) the solubilities of metals in the liquid, and to some extent in the solid state; (b) the relative freezing-point depressions and apparent molecular weights; (c) the ability of a molten metal to wet solid metal.

It is expected, also, that it will prove very significant in connection with another phenomenon now under investigation in this Laboratory, namely, the initial overvoltage required to start the deposition of one metal upon another.

Whenever it shall prove possible to predict the chemical combinations of metals with one another, this knowledge, together with Table VI, or a

¹⁶ THIS JOURNAL, 41, 1067 (1919).

perfected form of it, should make it possible to correlate completely all of the intermetallic systems.

Summary

- 1. Various means of estimating the relative internal pressures of metals are discussed and tables are given.
- 2. Data are given showing the correlation between these tables and the behavior of binary metallic solutions.

BERKELEY, CALIFORNIA

EXTREMELY DRY LIQUIDS

By GILBERT N. LEWIS RECEIVED AUGUST 13, 1923

The very important discoveries of Baker¹ concerning the boiling points and other properties of highly desiccated liquids have opened a large and most promising field of physicochemical investigation. The startling results which have already been obtained have aroused some degree of skepticism, because of a suspicion that they were irreconcilable with fundamental thermodynamic principles; but I am convinced that no essential conflict exists, and that the chief observations which have so far been made not only may be interpreted thermodynamically, but also permit, with the aid of thermodynamics, some valuable predictions.

At first the experiments seemed to indicate that the removal of the smallest traces of water produced profound changes in the static properties of a liquid, such as might be explained by a large shift of inner equilibrium through the formation of a larger number of complex molecules from simple molecules. Smits² believes that such a change in equilibrium is thermodynamically possible and that it is in fact the explanation of the facts observed by Baker.

With this conclusion I can by no means agree. It is not absolutely prohibited by the laws of thermodynamics alone, but any one who will read the chapter on dilute solutions in the recent treatise on thermodynamics by Professor Randall and myself will see how little is required, besides the laws of thermodynamics, to prove Raoult's law for the infinitely dilute solution. For solutions of moderate concentration its approximate validity has been attested by hundreds of observations of the most varied sorts. The only marked exceptions occur when the solute dissociates, and then the activity of the solvent is diminished two, three, or more times as much as Raoult's law predicts, according as the solute molecule dissociates into two, three, or more molecules. Smits' hypothesis seems

¹ Baker, Phil. Trans., 79A, 583 (1888); J. Chem. Soc., 65, 611 (1893); 81, 400 (1902); 91, 1862 (1907); 101, 2339 (1912); 121, 568 (1922).

² Smits, Proc. acad. Sci. Amsterdam, 26, No. 3 (1923).

to imply changes in the activity of the solvent which are thousands or millions times as great as those given by Raoult's law.

Therefore, I think we must conclude that the mere removal of the last traces of water from a liquid could not appreciably change the existing equilibrium between the several molecular species, which might be assumed to exist. If water acts as a catalyst for the process of interchange between one molecular species and another, its removal could only serve to "freeze" the already existing state of equilibrium, by inhibiting further interchange between the various forms.

Such a behavior is well known in the case of liquid sulfur which contains two distinct molecular species known as S_{λ} and S_{μ} , which probably have the formulas S_{δ} and S_{δ} . When the liquid sulfur contains a trace of a substance very similar to water, namely ammonia, there is rapid interchange between the two species, so that equilibrium follows rapidly upon any change of condition, and the substance behaves like an ordinary pure liquid. But if the trace of ammonia is removed, the change from one species to the other is inhibited, and the sulfur behaves like a mixture. For example, it does not freeze at a fixed temperature, but the temperature changes during the process of freezing.

Let us consider, as a simple case, a hypothetical liquid consisting solely of simple molecules A and complex molecules of a single molecular species B; and let us assume that in the presence of moisture complete equilibrium is instantly established between A and B. Also in the vapor phase we may assume the same equilibrium to exist, although here the proportion of complex molecules might be negligibly small. Essentially, therefore, we may postulate a liquid consisting of a mixture of molecules A and B, and a vapor consisting merely of molecules A, all in equilibrium with one another.

Let us now imagine the removal of the last traces of water, or other catalyst, so as to inhibit the reaction A \longrightarrow B, in either direction. If this should be done at constant temperature, the vapor pressure will be the same as before, as well as the proportions of A and B in the liquid. But, if the liquid is now heated, more of the A molecules will escape into the vapor phase, and eventually the liquid will consist almost entirely of molecules B. In order to boil this liquid, a temperature must be attained at which either the B molecules themselves vaporize, or the rate of formation of A from B, in spite of the absence of catalyst, is rendered appreciable by the increase of temperature. Both of these processes might occur simultaneously.

This view of the phenomenon is in complete accordance with the latest experiments of Professor Baker,³ carried out in coöperation with Professor Smits. It was found that a sample of carefully dried benzene, similar

³ Baker, J. Chem. Soc., 121, 568 (1922).

to those which had already shown abnormally high boiling points, could be fractionally distilled, like a mixture of two independent components, the temperature of a thermometer placed above the boiling liquid rising steadily throughout the course of the distillation.

It is conceivable that in some cases the process of fractionation might not be observable and the dried liquid might almost immediately exhibit a constant high boiling point. If in the equilibrium mixture the proportion of A molecules were very small, their distillation from the dried mixture might not be noticeable, and the liquid could be heated directly to the new boiling point at which the vapor pressure of the B molecules would be equal to the atmospheric pressure, or at which the transition from B molecules to A molecules would be sufficiently rapid to give in the vapor phase a mixture of the two species, such that their total pressure would be equal to the atmospheric.

All these considerations lead to the interesting prediction that we shall find liquids with abnormally low boiling points as well as those with abnormally high boiling points. For thermodynamics teaches us that anything which inhibits the reaction A \longrightarrow B in one direction must also inhibit it in the other direction, and if, therefore, we could obtain a liquid containing only A molecules, it might have a much lower boiling point than the normal liquid. Thus if the normal vapor consists almost entirely of A molecules we should be able, by passing the vapor through phosphorus pentoxide and then condensing it, to obtain a liquid of very high vapor pressure and correspondingly low boiling point.

It seems likely that experiments with dried liquids and vapor may be conducted without exorbitant expenditure of time. In Baker's experiments the liquids employed had been dried over phosphorus pentoxide through a period of years, but it is to be observed that he depended in the main upon a process of diffusion, or accidental convection, to bring the moisture to the surface of the phosphorus pentoxide, and it probably was necessary to remove the moisture not only from the liquid and vapor but also from the surface of his glass vessel. By employing specially treated glass or some less hygroscopic material for the vessel, and by providing a circulating system which would rapidly carry the material to be dried through the phosphorus pentoxide, it should be possible to lessen very greatly the time required for drying. If such experiments prove to be successful, it should be possible to obtain results more quantitative than any so far secured. Such quantitative results would then be amenable to the same sort of precise thermodynamic treatment which has already been accorded to the case of liquid sulfur.4

While I have assumed for the sake of simplicity that the absence of water
See Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York,
1923.

inhibits a single reaction between a simple molecular species A and a more complex molecular species B, we may anticipate that the actual facts will often prove to be far more complicated than this. There is nothing in the chemical properties of some of the liquids investigated by Baker to lead us to expect any one complex molecule to show exceptional stability. Rather we should expect the formation of double, triple, quadruple molecules, and so on, to be evidence of a tendency in the condensed liquid phase toward the formation of indefinite aggregates, perhaps not entirely dissimilar to those which are produced in the process of crystallization, or at least due to forces similar to crystalline forces in that they operate only between molecules which are brought into close proximity. These, however, are questions which it is hardly worth while to discuss until further experimental information is at hand.

While at present the above explanation of the peculiar properties of dried liquids is the only one consistent with thermodynamics that seems at all plausible, it must be confessed that some of the results obtained by Baker still seem a little mysterious. According to this explanation, the static properties of a liquid, when it is freed from the last trace of water at a fixed temperature, should remain essentially the same. By a static property I mean such a one as the volume, and indeed Baker has found that the density of liquids is the same after thorough drying.

Whether surface tension is to be regarded as a static property would depend upon its method of measurement. If the liquid is allowed to rise in a capillary, a process occurs which is analogous to the formation of a new phase, and the surface tension so measured need not be the same in the dried and the undried liquid. In fact, the results indicate that the surface tension so measured is higher in the dried than in the undried liquids but further experiments in this direction should be undertaken.

Baker has found that the color of liquid nitrogen trioxide changes when the last trace of moisture is removed. This might of course be explained by attributing a very high coloring power to the water itself, but it is conceivable that color itself is not a static property, and that the absorption of light is accompanied by a chemical process which does not occur in the absence of a catalyst.

Perhaps the most puzzling observations made so far are those concerning the freezing points of the dried liquids. In every case the freezing points of the dried liquids have proved to be higher than those of the undried. We know little regarding the mechanism of crystallization. It might have been expected that complex molecular species would crystallize more readily than the simple molecular species, but on the other hand the liquid complex may not be of the sort that would fit into the crystal structure, and if so it would be the simple molecules which would most readily take part in the process of crystallization. This appears

to be the case. If a liquid is dried at a certain temperature to the extent of inhibiting the interchange between simple and complex molecules, and the temperature is then lowered, there will be a larger proportion of simple molecules than there would be in the equilibrium liquid at this lower temperature. The simple species would therefore have a higher activity in the dried liquid, and if it is this species that crystallizes, freezing will begin at a higher temperature than in the case of the normal liquid. However, as the simple molecules crystallize the freezing point should drop, and indeed fall ultimately below that of the undried liquid.

Finally, it is to be remarked that if it is found by experiment that circulation of a liquid through phosphorus pentoxide does not give the same results that are obtained when the liquid stands over phosphorus pentoxide; and if at the same time it is found that the static properties of the dried liquid do differ materially from those of the undried, we should be forced to an explanation which at present seems rather unlikely. It would be necessary to assume that a liquid in the ordinary state is not in the condition of highest stability, but tends to go over on quiet standing to another condition, just as a finely divided precipitate tends to form a single perfect crystal, or as a drawn wire tends to assume a coarsely crystalline condition. If the liquid on standing over phosphorus pentoxide really assumes a more stable state, then the original state could not be restored merely by the addition of a trace of water, but some agitation of the liquid would also be required in order to furnish the necessary energy for the conversion of the liquid into its normal, less stable, state. However, there seems to be nothing in the present stage of the experiments which would indicate the need for adopting so bizarre a conclusion.

Summary

The remarkable effects produced by removing the last traces of water from liquids promise to furnish information of great value concerning the liquid state. The only plausible explanation of these effects that seems consistent with thermodynamics rests on the assumption that water is a catalyst for processes between various molecular states, and that its removal merely inhibits such processes. If this explanation is correct the process of drying only "freezes" an existing equilibrium and (at constant temperature) cannot alter the static properties of the liquid. This leads to interesting predictions, for example, that liquids will be found that exhibit abnormally low, as well as abnormally high boiling points.

Equitable Trust Company of New York 10 Moorgate London, England [Contribution from the Chemical Laboratory of the Johns Hopkins University]

MANGANESE DIOXIDE IN THE CATALYTIC OXIDATION OF CARBON MONOXIDE¹

By W. A. WHITESELL AND J. C. W. FRAZER RECEIVED AUGUST 15, 1923

Introduction

The preparation of active catalysts for the oxidation of carbon monoxide has raised many questions as to the mechanism of the reaction. As method of preparation, choice and manner of incorporation of promoters, physical conditions of the substances, treatment before use, and conditions under which the reaction is carried out seem to be influencing factors, it is necessary to investigate them before any comprehensive theory can be proposed with a measure of assurance.

The discovery and preparation of these oxidation catalysts has been described in an article by Rogers, Piggot, Bahlke and Jennings² and also by Scalione and Merrill.³ Further work done in this Laboratory is described by Lanning⁴ and English.⁵ Lanning investigated the adsorption isotherms of preparations of manganese dioxide and the catalyst, Hopcalite, composed of manganese dioxide and silver oxide, to obtain an idea of their structure and the effect on adsorption of the method of preparation and treatment of Frémy oxide and the method of incorporation of the promoters. He found that the substances were highly porous, with a large internal surface, the size of the pores approaching molecular dimensions, that water vapor was taken up by physical adsorption and not as hydrate, its poisoning effect being due to a reduction of the active surface, and an alkaline solution did not reduce the surface but very likely changed its character. The Frémy oxide and promoter oxides were found to be oppositely charged, thus helping to give mutual dispersion to a high degree.

English studied the oxygen pressure over these substances at various temperature and found that the dissociation pressures indicated the existence of solid solutions.

Plan of Work

The present investigation was undertaken as a continuation of the study of the mechanism of the reaction, by preparation in different ways of various oxides such as manganese dioxide, silver oxide, cupric oxide, cobaltic oxide, lead dioxide, nickelous oxide, ferric oxide, etc., and the quantitative study of their effects, separately at first and then in mixtures, on the oxidation of carbon monoxide, hydrogen and other convenient, oxidizable substances. As manganese dioxide seemed to be the essential constituent in all previously prepared highly active catalysts studied in this Laboratory it was studied first, with the result that the investigation was given a rather

- ¹ The substance of this article forms a part of the dissertation submitted by W. A. Whitesell for the degree of Doctor of Philosophy at Johns Hopkins University and the work was carried out at the suggestion of J. C. W. Frazer.
 - ² Rogers, Piggot, Bahlke and Jennings, This Journal, 43, 1973 (1921).
 - ³ Scalione and Merrill, ibid., 43, 1982 (1921).
 - ⁴ Lanning, Dissertation, Johns Hopkins University, 1920.
 - ⁵ English, *ibid.*, Johns Hopkins University, 1922.

different turn from that outlined, one result being the preparation of catalysts of manganese dioxide alone with equal if not greater activity than former oxide mixtures. They have functioned with 100% efficiency over a wide range of mixtures of carbon monoxide and air at temperatures as low as $-20\degree$.

Apparatus and Experimental Conditions

The apparatus and experimental conditions were essentially those described by Rogers, Piggot, Bahlke and Jennings.²

Experimental Part

The first experiment was made with a sample of commercial Frémy oxide which had been pressed, screened and dried in an air-oven overnight at 110°. As the results of this experiment determined in large measure the further course of the investigation, they will be given in some detail. The gases were first passed through soda lime and calcium chloride. The data are given in Table I.

Table I

Effect of Drying Temperature on Catalytic Behavior of Manganese Dioxide

Time of run, 1 hour. CO, 1 cc. per min. Air, 100 cc. per min.

Fresh sample.

				Time of r	un, 40 min.
Temp. °C.	Efficiency %	Temp. °C.	Efficiency %	Temp. °C.	Efficiency %
50	61	17	73	0	14.8
20	20	18	54	22	22.8
50	36	125	94	22	9.2
75	49	150	99	22	9.2
100	93	16	98	18	5.5

The temperature was then raised to 150° when considerable moisture came off of the catalyst and condensed in the exit tube. This was swept out with dry air. The temperature was then allowed to fall to that of the room when the efficiency was 95%. The hot zone appeared at the top of the catalyst bed but moved slowly to the bottom with a slight loss of efficiency in the course of 5 to 6 hours. While the gases continued to pass, the temperature was raised to 150° for several hours; the gases were then stopped and the tube cooled to room temperature. When the 1% mixture was then passed through, the hot zone appeared immediately at the top of the bed and practically complete oxidation occurred.

This series of runs brought out a number of points: (1) the poisonous effect of very small amounts of water vapor and perhaps of other adsorbed substances; (2) manganese dioxide as the primary substance in causing the oxidation, as had been previously thought; (3) manganese dioxide when suitably prepared is able to take up oxygen at a sufficiently elevated temperature to restore its activity at a lower temperature.

The material used in these experiments was the most active preparation of manganese dioxide previously described, and the results indicate that there is some temperature at which the rate of reoxidation is equal to the rate of oxidation of the carbon monoxide under the given conditions, that is some point at which this substance is just completely catalytic.

Inasmuch as impurities seem to play such an important part in the catalytic activity of many substances, it was thought that a purer sample of manganese dioxide might prove completely catalytic at ordinary temperatures. All previously prepared Frémy oxide had been made from potassium permanganate and sulfuric acid. It is difficult to wash sulfates from samples of manganese dioxide made in this way. As nitrates are less strongly adsorbed than sulfates it was thought the decomposition of permanganate in nitric acid might give a better product, and attention was turned in this direction. The idea proved very fruitful and resulted in the preparation of samples by methods which give very active catalytic oxides at temperatures as low as -20° . These methods are as follows.

- 1. Decomposition of potassium permanganate in concd. nitric acid. Powdered permanganate is poured into concd. nitric acid. Several hours are required for the decomposition of the permanganic acid and the mixture must be well stirred and cooled to prevent explosion. When these precautions are observed the decomposition goes smoothly and the danger is not great. A very black, finely divided, "sandy" product is obtained which can be washed and filtered rather easily. It must be pressed to secure necessary hardness as otherwise it dries to a sandy powder.
- 2. Retreatment of the commercial Frémy oxide. The moist oxide is treated with concd. nitric acid, diluted, washed, and filtered. It is best to allow the product to stand in contact with the acid solution for several hours and occasionally stir the mixture to keep the particles in suspension. This product dries fairly hard without being pressed, the precipitate being more gelatinous than that described in the preceding method.
- 3. Oxidation of manganese sulfate with potassium permanganate in nitric acid solution. Powdered permanganate or a concentrated solution is added to the equivalent amount of manganous sulfate in solution in nitric acid. This is a very rapid method of preparation, as precipitation of the dioxide is complete almost immediately. The product is of the same order of fineness as that described in the first method and must be washed, filtered and pressed in the usual way. The final washings are always made with distilled water.
- 4. Oxidation of manganous hydroxide precipitated from manganous sulfate. The hydroxide is precipitated from the sulfate solution by sodium or ammonium hydroxide and washed thoroughly. It may then be treated in two ways: (a) it may be dissolved in nitric acid and the solution evaporated,

the nitrate decomposing to the dioxide; care must be taken to avoid heating it too strongly as otherwise the product may become very dense and inactive, resembling the natural substance; the dry dioxide is then treated with concd. nitric acid, washed, and dried; (b) manganous hydroxide may be oxidized as far as possible in the air (this occurs most rapidly when the hydroxide is nearly dry) and then treated with concd. nitric acid which converts the brown hydrated oxide into a very black product that is washed and filtered in the usual way; it is unnecessary to press this material.

These samples are perfectly catalytic for the oxidation of carbon monoxide at ordinary temperatures, giving a sharp hot zone 0.5 cm. to 1.0 cm. wide at the top of the catalyst bed, which remains well defined after a continuous 20-hour run. When the drying tubes are removed the catalysts are rather rapidly poisoned by the moist gases and the activity is recovered extremely slowly at room temperature when the train is reconnected. It regains its activity immediately, however, when heated to about 150° in a stream of dry air. In fact, all the catalysts should be dried under these conditions before use. Above —20° pure carbon monoxide is oxidized quantitatively with corresponding reduction of the manganese dioxide to lower oxides of manganese. Using a 1 to 2% mixture of carbon monoxide in air, there is no induction period at the beginning of the reaction and complete oxidation occurs at once even at the low temperatures mentioned. An attempt was made to reduce the catalyst using carbon monoxide diluted with nitrogen, but so little reduction seemed to occur that it was investigated more closely, when it was found that the 2 to 3% of oxygen in the compressed nitrogen was being used up by the carbon monoxide, with little apparent reduction of the oxide occurring.

Adsorption of Carbon Dioxide and Carbon Monoxide

During the first experiment with a sample of preparation No. 1 the carbon dioxide was held back by adsorption so long that it was thought worth while to work out its isotherm at 0°.6 The data are given in the following table from which the curve has been plotted.

Table II
Adsorption of Carbon Dioxide by Manganese Dioxide at Zero Degrees

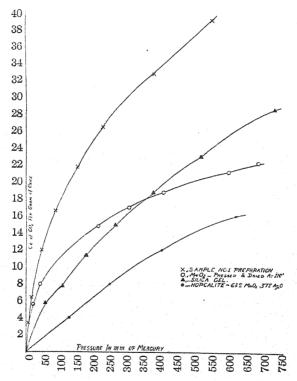
x/m = cc. Pressure of CO ₂ per Mm. of g. of oxide mercury	x/m = cc. of CO ₂ per g. of oxide	Pressure Mm. of mercury	x/m = cc. of CO ₂ per g. of oxide	Pressure Mm. of mercury
0.39 0.6	12.09	44.36	26.30	223.88
3.42 5.27	16.74	86.53	32.54	369.58
6.41 13.13	21.78	149.93	38.77	538.46

The sample had been dried at 180° for 3 hours in a stream of air over phosphorus pentoxide and then evacuated for $3^{1}/_{2}$ hours at 30° .

⁸ This work was done by Mr. Preston with the apparatus which is used in this laboratory for measuring adsorption.

Several of Lanning's curves are reproduced for the sake of comparison. These data show an unusually high adsorption of carbon dioxide by this particular sample, the curve lying entirely above that of silica gel even at the higher pressures. At lower pressures the amount taken up is twice that absorbed by silica gel or previous preparations of the sample or mixed oxides. This was rather surprising, as the sample was so "sandy" and non-gel-like in structure when precipitated. It thus shows a very large internal surface.

As it seemed likely that these catalysts were specific adsorbents for carbon monoxide, several attempts were made to test this experimentally.



Runs were first made to obtain an approximate idea of the rate of desorption of adsorbed carbon monoxide. Carbon dioxide was dried by calcium chloride and phosphorus pentoxide and then passed through a 3g. sample of the catalyst at -21° for 10 minutes at atmospheric pressure and at a rate of 30 cc. per minute. Then the train was closed at the exit end of the catalyst tube and left open to the carbon dioxide tank for 30 minutes. The train was then swept out with air at the rate of 30 cc. per minute until the atmosphere over the catalyst had been changed about twice, when bulbs containing 0.2034 N barium hydroxide solution were connected

with the apparatus and the amount neutralized was determined at various intervals

TABLE III

RATE OF	Desorption of	of Carbon	DIOXIDE FROM	MANGANESE	DIOXIDE
Temp., °C.	-15	-15	16	16	16-100
Time, min.	15	15	15	15	30
Ba(OH)2 neut. co	e. 10.9	1.8^{a}	2.0	0.7	0.9^{b}

^a Only a trace was then coming over, so the temperature was allowed to rise.

From this catalyst carbon dioxide is, therefore, desorbed much more readily and completely than from Hopcalite as found by Lamb, Scalione and Edgar. In Hopcalite it is most likely held chemically to some extent by the more strongly basic oxide promoters. Adsorption of carbon monoxide was tried at -20°, -15°, 0° and 20° with practically identical results. The procedure was as follows. Carbon monoxide diluted with nitrogen freed from oxygen by bubbling through alkaline pyrogallol was passed slowly over the catalyst. The amount of nitrogen was gradually cut down until pure carbon monoxide was being passed, when the train was closed off at the exit of the catalyst tube and left open to the carbon monoxide tank for one hour. Then the train was swept out slowly with oxygen-free nitrogen until the tube was filled with nitrogen when the rest of the train was connected. Nitrogen was passed first at the temperature of the experiment until desorption was complete and finally with the catalyst at 100°. In all cases carbon dioxide appeared in the barium hydroxide tube at about the same rate as in the previous desorption run with carbon dioxide. It was hoped that any carbon monoxide adsorbed would be desorbed as such and thus appear in the second barium hydroxide tube. The same results were obtained by the use of moist as with dry nitrogen during the desorption. After the catalyst has been reduced sufficiently, the carbon dioxide comes off more slowly and at a higher temperature, indicating probably the formation of unstable carbonates by the lower oxides of manganese. No monoxide appeared in the second barium hydroxide tube, showing that oxidation of the carbon monoxide had occurred before desorption from the catalyst. This will be discussed later.

Effect of Carbon Dioxide on the Catalysis

Several runs were made with mixtures of carbon monoxide, carbon dioxide and air to test for a possible poisoning effect of the carbon dioxide. These tests were made with a 3g. sample of preparation No. 3. Some of the typical data are given in the following table, which is self explanatory.

Analyses were made at 30-minute intervals when equilibrium appeared to have been reached, as the results could be checked rather closely.

^b Only the slightest trace was then retained.

⁷ Lamb, Scalione and Edgar, This Journal, 44, 744 (1922).

Table IV

Effect of Varying Partial Pressures of Carbon Dioxide on the Catalytic Oxidation of Carbon Monoxide

Temp.	CO Cc./min.	CO ₂ Cc./min.	Air Ce./min.	Remarks
0	1	1	100	100% oxidation
0	1	100	100	100% oxidation
0	1	100	50	100% oxidation
-15	1	25	100	100% oxidation
-15	1	35	100	Trace of CO passed
-15	2	35	100	Several % of CO passed
-20	1.2	60	60	80% oxidation ^a
-20	1.2	60	100	50% oxidation

^a At this point the CO₂ was shut off and the air-CO mixture was passed for 5 minutes. At the end of this time 100% oxidation was occurring. CO₂ was again turned on.

Analytical Data

Analyses of samples for adsorbed alkali and available oxygen are given below, results being the average of several determinations on the various preparations described above.

P_2O_5 at 180° for several hours 2 MnO _{1.908} Sample dried in an oven at 120° 3 MnO _{1.906} Wet sample 3 MnO _{1.808} 0.27 Sample dried as No. 1 above	Sample	Mn: O	K₂O %	Remarks
2 MnO _{1.908} Sample dried in an oven at 120° 3 MnO _{1.986} Wet sample 3 MnO _{1.808} 0.27 Sample dried as No. 1 above 5 MnO _{1.947} 1.75 Sample Hopcalite, 60% MnO ₂ - 40%	1	$MnO_{1.853}$	0.64	Samples dried in current of air over
3 MnO _{1.986} Wet sample 3 MnO _{1.808} 0.27 Sample dried as No. 1 above 5 MnO _{1.947} 1.75 Sample Hopcalite, 60% MnO ₂ - 40%				P ₂ O ₅ at 180° for several hours
3 MnO _{1.868} 0.27 Sample dried as No. 1 above 5 MnO _{1.947} 1.75 Sample Hopcalite, 60% MnO ₂ - 40%	2	$MnO_{1.908}$	• • • •	Sample dried in an oven at 120°
5 MnO _{1.947} 1.75 Sample Hopcalite, 60% MnO ₂ - 40%	3	MnO_{1-986}		Wet sample
	3 *	$MnO_{1.868}$	0.27	Sample dried as No. 1 above
CuO, dried in oven at 120°	5	$MnO_{1.947}$	1.75	Sample Hopcalite, 60% MnO ₂ - 40%
				CuO, dried in oven at 120°

Available oxygen was determined by the Bunsen method; this was found to be more rapid and satisfactory than the oxalic acid method. Total manganese was determined by means of sodium bismuthate, and potassium by precipitation with chloroplatinic acid.

Experiments with Hydrogen

In these experiments the water formed was collected in a weighed bulb of phosphorus pentoxide just after the catalyst tube. The total amount of hydrogen passed was obtained from the flowmeter readings. Inasmuch as the catalyst holds back water, especially at low temperatures, this method of procedure would not be so very satisfactory except for the fact that only slight oxidation appears to occur below 100–150°. Pure hydrogen does not reduce manganese dioxide at room temperature, judging from the absence of a heat effect. At 100°, 1 to 2% oxidation occurs and at 200° about 40 to 50%. Reduction of manganese dioxide by hydrogen begins at a higher temperature than in the case of Hopcalite, which con-

tains as high as 40% of the more easily reducible cupric oxide. This should make the manganese dioxide catalysts somewhat better for the removal of carbon monoxide from mixtures of this gas with hydrogen than Hopcalite under properly controlled conditions. Several qualitative tests have verified this.

Preparation of Cupric Oxide

Cupric hydroxide was precipitated from cupric nitrate solution with sodium hydroxide, and the precipitate washed thoroughly, pressed and dried. A sample of this oxidized 1 to 2% of a 1.0% mixture of carbon monoxide and air at room temperature but was not catalytic under these conditions.

Several experiments were made similar to those described for manganese dioxide to test for possible adsorption of carbon monoxide. Pure monoxide at the rate of 15 cc. per minute was passed over the catalyst for about 30 minutes at -20°, the train was swept out very thoroughly with nitrogen, and finally the barium hydroxide bulbs were connected. From an 8g. sample, between 0.8 and 4.0 cc. of carbon monoxide, calculated from the barium hydroxide neutralized, was desorbed and appeared in the second barium hydroxide tube. It was not expected that duplicate experiments on the same sample would agree closely, as the condition of the catalyst would be changed by its previous treatment. The carbon monoxide came off slowly at the low temperatures while no dioxide appeared in the first tube until nearly room temperature was reached. Then the adsorbed carbon dioxide came off until the final temperature of heating at 200°. From 8 to 20 cc. of dioxide was desorbed in this way from the 8g. sample during the different runs, showing that appreciable oxidation had occurred at the low temperatures, as was also shown by the appearance of carbon dioxide in the first tube during the time carbon monoxide was passing through the cupric oxide. Very likely, some carbon monoxide is oxidized in the process of desorption, so that the measured amount does not give the total monoxide held as such. Carbon dioxide is desorbed much less readily from this oxide than from the samples of manganese dioxide.

Discussion of Results

There are several points of interest which the present investigation has contributed in connection with the particular reaction studied, both to a knowledge of this reaction and the subject in general. From the results, it is clearly shown that manganese dioxide in Hopcalite mixtures is the initial cause of the oxidation, certainly at the lower temperatures. The active preparations are able to oxidize carbon monoxide extremely rapidly, either catalytically or at the expense of their own oxygen. The analytical data show that these active samples have a very low potash content, less than 0.5 to 1.0% of K₂O, while the partially active sample initially tried

contained very likely 3% or more, as has been shown by other investigators (English).⁵ These samples were otherwise quite alike as to physical structure. The commercial sample after partial reduction was able to take up enough oxygen at an elevated temperature to restore its activity for a time. When it was more completely freed from potash it was able to take up oxygen fast enough to become completely catalytic at lower temperatures. This points to a mechanism of alternate reduction and oxidation of the catalyst. The efficiency is quite evidently dependent on the nature of the active surface as well as on its extent. A sample of preparation No. 4, for example, which had been ignited too strongly, on evaporation became quite dense, resembling the natural product and was entirely inactive, although alkali free. This meant a packing and possibly a total change of structure of the material and a reduction and probably alteration of the nature of the surface but without destruction of the porous structure. The "promoted," Hopcalite, sample is active, although it still may contain 1.74% of K₂O. To state with certainty the effect of the cupric oxide on the mixture it would be necessary to have data on a sample of manganese dioxide containing this amount of alkali. If the alkali is all associated with the manganese dioxide, as the Hopcalite is 60% of manganese dioxide, the latter actually contains 2.90% of K₂O. As a sample of manganese dioxide containing this much impurity would hardly be completely catalytic alone it seems that the cupric oxide does show promoter action. It is still possible that it cuts down the adsorbed alkali or affects the way it is held so that its poisonous effect is annulled. On the other hand, both cupric and manganous ions are catalysts in other oxidation processes. These adsorbed ions may, therefore, act as oxygen carrier to the carbon monoxide. The activity seems to be intimately connected with the ability and rapidity with which the substance can take up oxygen, which may be caused by the rapid shifting of electrons in manganese atoms, so the poison or promoter may affect the stray field or the atomic or molecular configuration of the catalyst itself.

Attention is next called to the manganese-oxygen ratios in the samples. Here as in the previous investigations the loss of oxygen by manganese dioxide is noticed even at room temperatures and in a wet sample, indicating a dissociation pressure of oxygen in the pure manganese dioxide greater than the partial pressure of the oxygen in the atmosphere. English⁵ finds that these oxides behave as solid solutions, the oxygen pressure varying with the composition of the mixture; this is similar to the conclusions of Sosman and Hostetter⁸ in the case of the oxides of iron. The action of promoters and poisons may be due to their presence as constituents of such solutions. The fact that the mixtures lose oxygen at room temperature shows that they have a dissociation pressure greater than the oxy-

⁸ Sosman and Hostetter, This Journal, 38, 807 (1916).

gen in the air, and the activity because of this is greatly increased by the fineness of division of the particles. The molecules are at a point where electron changes occur with great rapidity and oxygen evaporates and condenses as readily as molecules do in the case of a liquid at its boiling point.

Water being a highly unsaturated substance with a strong field is readily adsorbed and is, therefore, a poison for many catalytic reactions. Carbon monoxide is often thought of as an unsaturated compound, but it has a weak stray field and molecules of stable configuration, as evidenced by its low boiling point and other physical properties. Yet in the catalysis of the reactions, $2H_2 + 0 \Longrightarrow 2H_2O$ and $N_2 + 3H_2 \Longrightarrow 2NH_3$, carbon monoxide is a poison because it is rather strongly adsorbed, although in the latter case the poison effect may be due to the formation of water by the reduction of the carbon monoxide by hydrogen. It reduces most metallic oxides at a lower temperature than hydrogen and in the case of manganese dioxide this difference in temperatures of reduction seems to be especially large. It is known that manganese dioxide catalyzes the reaction, $O_2 \Longrightarrow$ O + O, which fact together with the reasons outlined previously would account for the increased activity of the oxygen. The low temperature of oxidation of carbon monoxide as compared with that for the oxidation of hydrogen points, however, to the activation of the carbon monoxide as an important factor. Taylor and Burns9 point out the importance of specific adsorption in the case of metallic catalysts. They say,

"Some metals, which show specific adsorption for carbon monoxide hold it very tightly. Maximum catalytic activity does not occur at temperatures at which maximum adsorption is shown. Free evaporation of reactants and resultants is necessary. It seems likely that any substance which can distort or disarrange the stable configuration of the molecule or arrangement of outer shell electrons will greatly increase reactivity."

The rapidity of oxidation of carbon monoxide (the time of contact is of the order of 0.01 second, comparable to that in the oxidation of ammonia) shows that the monoxide is not held very tightly as such. If it were, it would be its own poison. Failure to effect desorption of carbon monoxide as such from manganese dioxide points to a rapid rearrangement and reaction. That carbon monoxide may be adsorbed is shown by the experiments with the less active cupric oxide. The course of the reaction would be, then, adsorption and simultaneous oxidation of carbon monoxide by the catalyst; desorption of the carbon dioxide or its adsorption by capillary condensation in case the catalyst were not already saturated; and finally reoxidation of the catalyst. The carbon dioxide is inert and chemically inactive and therefore does not poison the catalyst except by mechanically covering the surface and preventing contact of the reactant with the catalyst surface.

⁹ Taylor and Burns, This Journal, 43, 1273 (1921).

The range through which molecular forces may act is variously put at 1 to 1500 $\mu\mu$. Assuming it to be near the larger limit it might not be necessary to postulate actual contact of the gas molecules and catalyst surface. The field of force might be strong enough at some distance to bring the gases into a reactive condition. Adsorbed poisons would modify or annul this stray field. The effect of temperature in altering the distance through which these molecular forces may exert themselves might conceivably have considerable influence on the temperature coefficients of chemical reactions.

Since this work was completed, two articles have appeared by Benton, ¹⁰ one on "Adsorption of Gases by Oxide Catalysts," and the other on "Adsorption and Catalysis in Carbon Monoxide Oxidations." This author proposes a mechanism for the reaction practically identical with that arrived at as a result of this investigation. This would indicate that oxidation of the carbon monoxide was caused by the oxygen of the catalyst, and that subsequently oxygen was taken up by the catalyst.

He described his manganese as a product of "high purity" and low density. Such a sample should have been very active according to the results recorded in the present investigation, but his results show that this was not the case and it still contained, very likely, several per cent. of impurities. The experience of the present writers has been that each preparation must be treated as a special case without assuming too much from previous work done on other preparations, unless accurate analytical data are available for comparison.

Summary

- 1. Methods for the preparation of active samples of manganese dioxide for the catalytic oxidation of carbon monoxide have been described.
- 2. Analytical results show that the amount of impurities, such as adsorbed alkali, plays an important part in the activity of these catalysts.
- 3. Experiments show a considerable temperature interval between the points required to oxidize hydrogen and carbon monoxide by these samples of active manganese dioxide.
- 4. A dynamic method for measuring the adsorption of carbon monoxide by manganese dioxide shows that it is desorbed from the catalyst as carbon dioxide.
 - 5. A mechanism for the reaction is proposed and discussed.

 BALTIMORE, MARYLAND

¹⁰ Benton, This Journal, 45, 887 (1923).

[Contribution from the Physical Chemistry Laboratory, The State University of Iowa]

THE FREE ENERGY OF DILUTION AND THE ACTIVITY OF THE IONS OF HYDROGEN IODIDE IN AQUEOUS SOLUTION¹

By J. N. Pearce and A. R. Fortsch Received August 16,1923

The free-energy decrease accompanying the transfer of one mole of salt from any concentration c_2 to concentration c_1 is most conveniently determined by the electromotive-force method. The free-energy decrease $(-\Delta F)$ and the electromotive force E are related to the activities of the ions by the well-known thermodynamic expression, $(-\Delta F) = e.m.f. =$ $RT \log \frac{a_2^+ \cdot a_2^-}{a_1^+ \cdot a_2^-}$, where a_2^+ , a_2^- and a_1^+ , a_1^- represent the activities of the cation and anion in concentrations c_2 and c_1 , respectively. The other symbols have their usual significance. If we now choose one solution so dilute, that we may assume the activity product, a_1^+, a_1^- , equal to the product of the concentrations of the ions as measured by conductance, then it is possible to calculate the product of the activities of the ions, a_2^+, a_2^- , at any other concentration c_2 from purely electromotive-force data. If we assume with MacInnes2 the hypothesis of the independent activity of the ions and also that in any solution of potassium chloride the activities of the potassium and chloride ions are equal, the expression $\sqrt{a_{K}^{+}.a_{Cl}^{-}}$ gives us directly the activity of either of these ions. Likewise, having determined by electromotive force the activity product of the ions for a given concentration for any other binary electrolyte containing either a potassium or a chloride ion, the ratios, $(a_{\rm M}^+, a_{\rm Cl}^-)/a_{\rm Cl}^-$ or $(a_{\rm K}^+, a_{\rm X}^-)/a_{\rm K}^+$ give immediately the activities, $a_{\mathbf{M}}^{+}$ or $a_{\mathbf{X}}^{-}$, respectively.

Adopting this procedure, Pearce and Hart³ have found that the activities of the chloride and bromide ions are equal for equal concentrations of their binary salts. It should be said in passing that we are not unmindful of the excellent work of Lewis and Randall.⁴ These men have calculated the same results for these ions from freezing-point and vapor-pressure data. For the sake of brevity, however, the discussion of their work as well a that of others will be omitted at this time. The present paper deals with a study of the free energy of dilution and the activities of the ions in aqueous solutions of hydrogen iodide.

Apparatus and Materials

The cell used was similar to that described by Linhart.⁵ The platinum wire anode

¹ This paper contains the essential parts of a dissertation by Dr. A. R. Fortsch.

² MacInnes, This Journal, 41, 1086 (1919).

³ Pearce and Hart, ibid., 43, 2483 (1921).

⁴ Lewis and Randall, ibid., 43, 1112 (1921).

⁵ Linhart, ibid., 41, 1175 (1919).

was tightly packed with fine, electrolytically deposited crystals of metallic silver and then covered with a layer of silver iodide. The silver iodide was prepared by precipitation from carefully recrystallized silver nitrate and potassium iodide; it was then washed with conductivity water until the washings gave no test for iodides and finally stored under conductivity water. Every possible care was taken throughout the work to exclude light, and in no experiment did the precipitate darken perceptibly. Two hydrogen electrodes were placed in each cell. These consisted of large pieces of platinum gauze heavily coated with platinum black. The hydrogen iodide was made by passing hydrogen sulfide through an aqueous suspension of pure resublimed iodine. The solution was boiled to remove the last traces of hydrogen sulfide and then fractionally distilled. The fraction of constant boiling point was stored over a small quantity of red phosphorus and was freshly distilled in a current of pure hydrogen when needed.

In making the solutions of hydrogen iodide, approximately the required volume of the constant-boiling acid was added to a given volume of cooled, previously boiled conductivity water. The cell and contents were repeatedly rinsed with the solution and then filled to the proper volume, the electrodes were inserted and the cell was placed in a large constant-temperature oil-bath. Hydrogen, obtained by the electrolysis of a strong solution of sodium hydroxide, was first passed through a strong alkaline solution of pyrogallol, then through concd. sulfuric acid and, finally, through saturator bulbs, containing an acid of the cell concentration into the cell. In preliminary experiments it was found that the rate of bubbling may be varied between 30 and 250 bubbles per minute without affecting the constancy of the voltage readings. The rate of flow was limited in every experiment to about 60 bubbles per minute. The time required for the cell to attain equilibrium under the precautions necessary varied from 4 to 8 days, depending on the concentration. The exact molal concentration of the hydrogen iodide was determined gravimetrically as silver iodide after the cell potentials had been read.

Accuracy of Method All electromotive-force data given in the following tables are the mean

values for at least two different arrangements of the cell. Readings were taken on the two hydrogen electrodes independently and unless the variation between the two was less than $0.04~\rm mv$. the process of preparation was repeated. All potential readings were corrected by applying the usual formula: $E = \frac{0.0001983T}{2}\log\frac{760}{x}$, where E is the correction voltage, T the absolute temperature and x the partial pressure of the hydrogen above the solution. All barometer readings were from a standard precision barometer and were corrected for latitude, altitude and temperature. The electromotive forces were read at 25°, 30° and 35°, in the order named, and then to ascertain whether any changes had occurred within the cell during the experiment the temperature was lowered to 25° and the readings were again taken. In only one cell (0.24608~M) did the initial and final readings at 25° differ by more than a few tenths of a millivolt.

In the preliminary work it was observed that the potential readings begin to vary considerably when the electrodes were allowed to remain in the solution for more than 60 hours. Upon removing the electrodes, allowing them to stand in nitric acid for an hour or more and then replatinizing them. readings could be duplicated indefinitely to within 0.10 mv. At 0.12972 M a slight opalescence was observed on adding a soluble chloride to the nitric acid wash water. At concentrations greater than 0.24608 M the amount of silver deposited on the electrodes became considerable and no consistent readings were obtainable.

The potential readings were made on a standard potentiometer, the reference standard being a certified Weston cadmium cell (1.01871 volts at 23°). The temperatures were accurately controlled to $\pm 0.03^{\circ}$.

Experimental Part

Table I gives the final values for the electromotive forces of the cells at various concentrations and at 25°, 30° and 35°.

Table I

ELECTROMOTIVE FORCES OF THE CELLS

Holder Agilag

	112 111, 1181 118							
1000 g.	E_{25} volts	E_{30} volts	E_{35} volts					
0.24608	-0.06905	-0.06864	-0.06829					
.12972	03615	— .03556	03531					
(.10000)	— .02273	02202	02162					
.07914	01210	01128	— .01073					
.05049	+ .01006	+ .01128	+ .01235					
.01981	+ .05735	+ .05931	+ .06083					
.01045	+ .08825	+ .09060	+ .09262					
.00505	+ .12417	+ .12707	+ .12964					
(.00500)	+ .12453	+ .12744	+ .13991					

The values of E (in parentheses) for the concentration 0.005 M were obtained by assuming E as a quadratic function of c, using the three concentrations 0.01981, 0.01045 and 0.00505. Those for the 0.10 M were obtained in a similar way by using the concentrations 0.24608, 0.12972 and 0.07914. It will be noted that a change of sign occurs between the concentrations 0.07914 M and 0.05049 M. This is due doubtless to the fact that silver iodide is extremely insoluble; a small concentration of hydrogen iodide is sufficient by reason of the common ion effect to reduce the concentration of the silver ion to such an extent that the potential of the cell is reversed.

The free-energy decrease $(-\Delta F)$ accompanying the cell reaction was obtained by multiplying the electromotive force of the cell by 96494. These values have been calculated for the various cells at the three temperatures, and from them we have calculated the temperature coefficients of free energy, α and β . The decrease in heat content $(-\Delta H)_{25}$ was computed by means of the relation: $(-\Delta H)_{25} = (-\Delta F)_{25}(1-298.09\alpha)$. This is obtained by substituting the expression for $(-\Delta F)$ as a function of the

temperature in the fundamental thermodynamic equation, $\frac{d}{dT}\left(\frac{-\Delta F}{T}\right) =$

 $\frac{-\Delta H}{T^2}$, performing the differentiation indicated and rearranging terms. The data thus assembled are collected in Table II.

Table II
The Free-Energy Decrease and the Heat-Content Decrease Accompanying the
Cell Reaction at 25°

1000 g.	$(-\Delta F)_{25}$ joules	α.10 ⁶	β.10 ⁷	$(\Delta H)_{25}$ joules
0.24608	- 6663	-1277	+ 177	-9199
.12972	- 3488	- 4211	+1886	-7867
(.10000)	- 2193	- 7609	+2726	-7168
.07914	- 1167	-16151	+4453	-6789
.05049	+ 970	+25909	-3092	-6524
.01981	+5534	+ 7608	-1539	-7016?
.01045	+ 8515	+5699	- 748	-5953
.00505	+11982	+ 4950	- 531	-5699
(.00500)	+12016	+ 4950	- 549	-5715

It will be noted that the values of α and β change sign between the concentrations 0.05049 M and 0.07914 M. At some concentration between these the electromotive force and hence the free-energy decrease are zero. Thus, the values of α must change from a small negative number to an infinitely large negative number on the one hand, and from an infinitely large positive to a small positive number on the other hand. In other words, the coefficient α changes sign by passing through infinity. The negative values of $(-\Delta H)_{25}$ decrease regularly with increasing dilution.

The decrease in free energy attending the transfer of one mole of hydrogen iodide from any concentration c to one exactly 0.005 M was obtained by the algebraic addition of the $-\Delta F_{25}$ values given in Table II. By sub-

stituting these values in the expression,
$$-\Delta F_{25} = RT \ln \frac{c_2^2 (\alpha_2^+, \alpha_2^-)}{c_1^2 (\alpha_1^+, \alpha_1^-)}$$

and assuming that the value of (a_1^+, a_1^-) for 0.005~M hydrogen iodide is the same as that determined by Noyes and MacInnes⁶ for the same concentration of hydrogen chloride, namely, 0.9312, we have calculated the product of the activity coefficients of the two ions at the remaining concentrations. Lewis and Randall⁴ have used as the basis of their values for hydrochloric acid a method of extrapolation described by Linhart.⁵ The value of the product of the activity coefficients for a 0.005~M solution is 0.8968. We have calculated the product of the activity coefficients using both values; the results are assembled in Table III.

From the data of Noyes and MacInnes⁶ on hydrochloric acid it may be noted that there is a minimum value for the activity-coefficient product at about 0.5 M. From this investigation we are led to the conclusion that the same type of variation is exhibited by the activity coefficients of hydri-

⁶ Noyes and MacInnes, This Journal, 42, 239 (1920).

TABLE III

The Free-Energy Decrease Attending the Transfer of one Mole of Hydrogen Iodide from Concentration ϵ to 0.005 M, and the Products of the Activity Coefficients of the Ions

с 1000 g.	$-\Delta F_{25}$ joules	α_{H}^+ , α_{I}^- (N-M)	$\alpha_{\mathrm{H}}^{+}.\alpha_{\mathrm{I}}^{-}$ $(L-R)$
0.2408	18679	0.7201	0.6857
.12972	15504	.7199	.6856
(.10000)	14209	.7185	
.07914	13184	.7585	.7223
.05049	11046	.7865	.7491
.01981	6482	.8111	.7724
.01045	3501	.8751	.8331
.00500	0000	.9312	.8968

odic acid, but that the minimum occurs at a lower concentration, about 0.11 M. We next plotted the activity-coefficient products against the concentrations on a large scale and read from the smooth curve the activity products at round concentrations. The geometric mean activity coefficients of the ions have been calculated and are tabulated for comparison along with the corresponding coefficients of the ions of hydrochloric acid as calculated on the assumptions of Noyes and MacInnes and of Lewis and Randall in Table IV.

Table IV
The Geometric Mean Activity Coefficients at Round Concentrations

1000 g.	HI (exp.)	HCl (N—M)	HI (exp.)	HCl (L—R)
0.005	0.965	0.965	0.947	0.947
.010	.937	.932	.920	.924
.020	.901	.899	.886	.894
.030	.893	.880	.877	
.050	.884	.855	.868	.860
.100	.862	.847	.846	.814
.200	.849	.796	.834	.783

It is evident from the data here given that the activity coefficients and the activities of the iodide and chloride ions are equal for any concentration of their acids up to $0.05\,M$. It is interesting to note that the activity coefficients, based on the assumption that the activity coefficient of $0.005\,M$ hydrochloric acid is 0.965, agree closely with the fractional ionization of uni-univalent salts of the type KCl as calculated by Randall. In regard to the different values of the activity coefficients obtained by using different values for the coefficient of the dilute solution arbitrarily chosen for reference, it is apparent that the difference lies mainly in the value of the reference chosen. Any error in either standard would influence the entire series of activity coefficients.

⁷ Randall, This Journal, 38, 790 (1916).

Summary

- 1. The electromotive forces of cells of the type, $H_2 \mid HI(c)$, $AgI \mid Ag$, have been measured at 25° for various concentrations of hydrogen iodide.
- 2. The free-energy decrease and the heat-content decrease attending the cell reaction have been calculated.
- 3. The free-energy decrease accompanying the transfer of one mole of hydrogen iodide from the various concentrations to a concentration exactly $0.005\ M$ has been computed. From these values we have calculated the geometric mean activity coefficients of the ions of hydrogen iodide, and we have found that for concentrations up to $0.05\ M$ these coefficients are practically equal to the corresponding coefficients for hydrogen chloride at the same concentrations. Obviously, the activities of the iodide and chloride ions are equal when in equivalent concentrations of their salts.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

THE DIFFUSION OF HYDROGEN THROUGH METALS1

By Horace G. Deming and B. Clifford Hendricks

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Deville and Troost,² Graham,³ Sieverts,⁴ and Charpy and Bonnerot⁵ have studied the diffusion of hydrogen through platinum, iron, palladium, copper and nickel. The rate of diffusion, found to be very different for different metals, was shown to increase rapidly with increasing temperature, but the results obtained were hardly more than qualitative, and were not expressed in terms that may be compared with recent work. More accurate data have been obtained by Schmidt⁶ and by Holt⁷ on palladium, by Richardson and coworkers⁸ on platinum, and by Edwards and Pickering⁹ on rubber, the rate of diffusion of hydrogen through these substances at different temperatures being shown graphically. In the work described in the present paper a method has been developed that permits the rate of diffusion of gases through metals to be determined under more precisely controlled conditions than has previously been possible; and preliminary

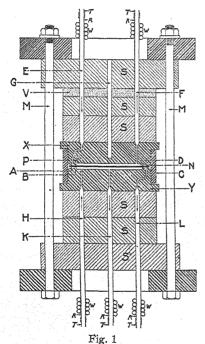
- ¹ Abstract of a thesis presented by B. Clifford Hendricks to the Graduate College of the University of Nebraska in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.
 - ² Deville and Troost, Compt. rend., 56, 977 (1865); 57, 965 (1863).
 - ³ Graham, Phil. Mag., [4] 32, 503 (1866).
 - 4 Sieverts, Z. physik. Chem., 60, 129 (1907).
 - ⁵ Charpy and Bonnerot, Compt. rend., 156, 394 (1913).
 - ⁶ Schmidt, Ann. Physik, [IV] 13, 767 (1904).
 - ⁷ Holt, Proc. Roy. Soc., 91A, 148 (1915).
 - 8 Richardson and others, Phil. Mag., [6] 8, 1 (1904).
 - ⁹ Edwards and Pickering, Bur. Standards Sci. Paper, 387, 346 (1920).

results have been obtained for the rate of diffusion of hydrogen through nickel, copper, lead, zinc and aluminum.

Apparatus

In designing the apparatus to be used in this work it seemed desirable: (1) that the metal to be tested should be in the form of flat sheets or discs; (2) that one metal should be easily interchangeable for another at the end of a series of tests; (3) that diffusion should be limited to a definitely measurable area; (4) that the temperature over this area should be as uniform as possible; (5) that the apparatus should be usable up to temperatures of at least 1000°. The method finally developed met these five requirements quite perfectly, the essential parts of the "diffusion-unit" being as shown in Fig. 1.

The metal to be tested was a disk D, about 9.5 cm. in diameter, of any desired thickness. This was clamped between two cylindrical steel blocks XY, each delimited



by two concentric circular knife-edges AB, and centered by a steel ring C. Bolts MM', passing through insulating soapstone blocks S and an asbestos ring V, served to draw the circular knife-edges against the metallic disk, but not necessarily tight enough to make a gas-tight joint.

Each steel block was tapped to receive three threaded steel tubes, joints being made gas-tight with metaphosphoric acid. Through one of these tubes, H, hydrogen, purified as described hereafter, was admitted to the shallow cavity in the upper surface of the lower steel block Y. The annular channel between the two knife-edges of this block was connected, through L with a vacuum pump, in order that any hydrogen leaking outward past the inner knife-edge might be immediately removed. The area of metal exposed to diffusion was thus definitely restricted to that circumscribed by the inner knife-edge of the lower block. This was 46.03 sq. cm. at 20°, becoming greater by about 0.2% at 100°, 1.2% at 500°, and 2.6% at 750°, on account of the expansion of the steel.

Any hydrogen diffusing through the given area of the metallic disk D was immedi-

ately swept out through F by a current of nitrogen which was admitted to the upper block through the tube E and the capillary opening P. This nitrogen also had direct access to the annular space N between the two knife-edges of the upper block and, being there maintained under a slight pressure, served to prevent the loss by leakage outward under the knife-edges of the upper block, of any hydrogen that might have diffused through the disk. By maintaining a brisk current of nitrogen through the upper portion of the apparatus it was possible to keep the hydrogen there at a very low concentration, and thus make sure that no appreciable part of the hydrogen diffusing through the disc should afterward be lost by being absorbed by the steel of the upper block or outlet tube.

The opening G served to admit a Chromel-Alumel thermocouple; K served as an outlet, when the chamber in the lower block was swept out with nitrogen, in preparing for a "blank determination." Connections were made outside the furnace in which the steel "diffusion unit" was heated, by tinning the steel tubes, and soft-soldering to platinized Pyrex glass. The soldered joints were water-cooled at higher temperatures.

Surrounding the steel blocks of the "diffusion unit" was a heating unit. The thermocouples, calibrated at the freezing points of tin, zinc, antimony and sodium chloride, 11 showed the temperature within the two steel blocks to be uniform, within 5°.

Connected to the tube F, Fig. 1, was a small electrically-heated furnace, containing copper oxide. This was kept at a dull red heat; and the water vapor, produced by oxidation of the hydrogen which had diffused through the metallic disk, was absorbed in phosphorus pentoxide and weighed.

Manipulation

In beginning each experiment, the "diffusion unit" was first heated slowly to the desired temperature, with the shallow chambers above and below the metallic disk filled with nitrogen, to prevent oxidation. Then a "blank determination" was made, to determine whether there was any change in the weight of the U-tubes containing phosphorus pentoxide when no hydrogen was being admitted to the "diffusion unit." In practice, an increase in weight of 1 or 2 mg. was obtained in the blank test, in several hours' run. Hydrogen was admitted to the lower chamber after preliminary blanks were secured, and measurements were then made at various temperatures which gradually approached the melting point of the sample under examination. Finally, the hydrogen in the lower chamber was displaced by nitrogen, in order that the series of measurements might be concluded with a second "blank determination."

The hydrogen was generated in a Kipp apparatus from zinc and dil. sulfuric acid, and purified by being passed successively through an alkaline potassium permanganate solution, a 5% silver nitrate solution, concd. sulfuric acid, a small electric furnace charged with copper turnings and heated to about 350°, and U-tubes containing soda-lime and calcium chloride. The nitrogen was obtained from a commercial cylinder, and was purified by being passed through an apparatus containing ammoniacal ammonium chloride solution to absorb oxygen.¹³ From this it entered a gasometer, displacing dil. sulfuric acid, and was subsequently purified by being passed through concd. sulfuric acid, a furnace containing copper oxide and copper

¹⁰ McKelvy and Taylor, This Journal, 42, 1366 (1920).

¹¹ Bur. Standards Circ., 35 (1919).

¹² In the results submitted, these "blank" values, which are probably due to moisture from the copper oxide and from hydrogen adsorbed by the steel blocks of the diffusion units, are not satisfactory. This is one procedure of this research which the junior author hopes to refine in work now under way.

¹⁸ Badger, J. Ind. Eng. Chem., 11, 1052 (1919); 12, 161 (1920).

turnings heated to about 350°, and finally through U-tubes containing soda-lime and calcium chloride.

Experimental Results

Aluminum.—The aluminum used was a disk of commercial sheet metal, 0.637 mm. thick. After a few preliminary determinations, to standardize the manipulation, the data given in Table I were obtained. The water collected in the blank determinations, expressed in milligrams per hour was, on the average, practically the same as when hydrogen was admitted to the lower chamber of the "diffusion unit." Thus, aluminum appears to be totally impermeable to hydrogen at temperatures as high as 550°. The hydrogen appeared to produce no great alteration in the physical properties of the aluminum, except that minute blisters appeared, forming parallel streaks across the surface of the metal, doubtless due to bubbles of gas trapped just beneath the surface, and elongated during rolling.

Table I

Diffusion of Hydrogen through Aluminum

Disk, 0.637 mm. thick. Area exposed to diffusion, 46.7 sq. cm.

Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	
5.9	510	8.2	1.4	Blank
2.4	540	1.8	0.7	Determination
4.4	540	4.1	0.9	Determination
1.03	575	0.6	0.6	Determination
2.3	550	4.9	2.1	Blank
1.01	570	0.7	0.7	Blank

Average blank, 1.4 mg. of water per hour. No detectable diffusion at temperatures around 550°.

Zinc.—The zinc used was a sample of Horse Head Brand, supplied by the New Jersey Zinc Company, stated to be about 99.5% pure, and containing at most 0.5% of lead and 0.011% of iron. The disc had an average

Table II

Diffusion of Hydrogen through Zinc

Disk, 1.643 mm. thick. Area exposed to diffusion, 46.7 cm.

Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	Hydrogen per sq. cm. per hr. Mg.
$3.7 \cdot$	260	1.7	0.46	Blank
2.0	255	1.4	.70	0.0008
2.0	262	1.0	. 50	.0004
4.5	310	3.8	.84	.0012
3.05	375	2.0	.66	.0008
6.1	380	4.1	.67	.0008
2.0	385	0.5	.25	Blank

Average blank, 0.35 mg. of water per hour.

thickness of 1.643 mm. Discarding a few experiments in which the time of diffusion was only two hours or less, the data obtained are given in Table II. The figures in the last column are obtained by correcting the data in the fourth column for the average rate of collection of water in the two blanks. The area exposed to diffusion in the temperature range studied was taken as 46.7 sq. cm.

Assuming the rate of diffusion to be inversely proportional to the thickness of the metal disk (Fick's law) we may calculate the specific diffusion rate of hydrogen through zinc, expressed in mg. per hour per sq. cm. area per mm. thickness, to be about 0.0012 at 375° .

Lead.—A disk of commercial soft lead was used, with an average thickness of 0.862 mm. The data obtained are given in Table III. The two preliminary blanks were unusually high, presumably due to incomplete drying of the copper oxide in the combustion furnace. If we assume that the first few determinations are vitiated by the same cause, we nevertheless have evidence from the remaining data of an extremely slight permeability of lead to hydrogen. We may calculate the specific diffusion rate of hydrogen through lead (mg. per hour per sq. cm. per mm. of thickness) to be not more than 0.001.

Table III

DIFFUSION OF HYDROGEN THROUGH LEAD

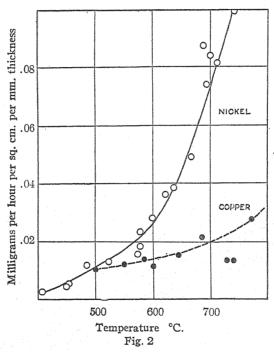
Disk, 0.862 mm. thick. Area exposed to diffusion, 46.7 sq. cm.

Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	Hydrogen per sq. cm. per hr. Mg.
1.5	185	1.4	0.9	Blank
1.5	210	1.2	.8	Blank
2.5	250	1.0	.4	Rejected
2.6	270	1.3	.05	Rejected
1.5	255	0.6	.4	0.0005
1.5	265	.9	.6	.0009
1.5	280	1.1	.7	.0014
1.25	295	0.3	.2	Blank
1.0	300	.0	.0	Blank

Blank correction in this series taken as 0.2 mg. of water per hour. Average rate of diffusion in three final determinations, 0.0009 mg. of hydrogen per sq. cm. per hour at temperatures around 265° .

Copper.—The data obtained with copper at first were very erratic. The metal appeared to be much more permeable to hydrogen than any of those previously examined. But after the metal had been exposed in the furnace to alternate heating and cooling for a number of hours, the rate of diffusion suddenly seemed to increase enormously. Microscopic examination showed a decided increase in the size of the metallic crystals, and the development of intra-crystalline cracks, as a result of the heating. In addition, the disk was perforated by several minute holes immediately above the hydrogen inlet.

It was presumed that a part of the difficulty might have been due to the reduction, by the hydrogen, of the cuprous oxide which is an impurity in ordinary copper. For this reason subsequent tests were made on sheet copper¹⁴ which had been made by cold-rolling cathode copper. Care was also taken to begin the observations at a high temperature, and to make successive determinations at lower and lower temperatures, without permitting the furnace to cool until the end of the series. In this way the alternate contraction and expansion of the copper disk, caused by repeated



heating and cooling, were avoided, and the tendency to form intra-crystalline cracks was minimized. Under these conditions the data given in Table IV were obtained. A rapid increase in permeability with increasing temperature is indicated, as shown graphically in Fig. 2. The specific diffusion rate of hydrogen through copper (mg. per hour per sq. cm. per mm. of thickness) may be calculated to be about 0.028 at 770° and about 0.011 at 500°.

Nickel.—Of the five metals studied, nickel was the easiest with which to work. The sample was of electrolytically refined nickel, 16 and had an aver-

¹⁴ Furnished by the American Brass Company.

¹⁵ A similar precaution was found to be necessary in work done by Richardson and coworkers (Ref. 8) on platinum.

¹⁶ Furnished by the International Nickel Company.

Table IV

Diffusion of Hydrogen through Copper

Disk, 0.391 mm, thick. Area exposed to diffusion, 46.7 sg. cm.

Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	Hydrogen per sq. cm. per hr. Mg.
1.0	730	0.6	0.6	Blank
.5	730	7.2	14.4	0.034
.8	737	11.4	14.3	.034
.6	770	19.3	32.2	.072
.5	687	11.8	23.6	.056
.5	645	8.7	17.4	.042
.7	605	8.4	12.0	.028
.5	585	7.6	15.2	.036
.6	550	8.2	13.7	.032
.5	500	5.6	11.2	.027
1.9	538	0.2	0.1	Blank
1.25	475	.2	.2	Blank

Average blank, 0.3 mg. of water per hour.

age thickness of 0.653 mm. This was under observation for a total of more than 90 hours, and was repeatedly heated and cooled, without showing any of the tendency to crack that appeared in the case of copper. A few of the

Table V

Diffusion of Hydrogen through Nickel

Disk, 0.653 mm. thick. Area exposed to diffusion, 46.7 sq. cm.

3.5 613 1.3 0.4 Blank 2.5 595 3.0 1.2 Blank 1.0 580 16.1 16.1 0.036 0.7 580 9.3 13.3 .029 3.17 575 34.8 11.0 .024 2.0 625 48.1 24.0 .056 1.5 665 47.6 31.7 .074 2.9 695 138.3 47.6 .114 1.07 710 56.4 52.7 .124 0.8 690 45.2 56.5 .133 3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020	Time Hrs.	Temperature °C.	Total water collected Mg.	Water per hour Mg.	Hydrogen per sq. cm. per hr. Mg.
1.0 580 16.1 16.1 0.036 0.7 580 9.3 13.3 .029 3.17 575 34.8 11.0 .024 2.0 625 48.1 24.0 .056 1.5 665 47.6 31.7 .074 2.9 695 138.3 47.6 .114 1.07 710 56.4 52.7 .124 0.8 690 45.2 56.5 .133 3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 <t< td=""><td>3.5</td><td>613</td><td>1.3</td><td>0.4</td><td>Blank</td></t<>	3.5	613	1.3	0.4	Blank
0.7 580 9.3 13.3 .029 3.17 575 34.8 11.0 .024 2.0 625 48.1 24.0 .056 1.5 665 47.6 31.7 .074 2.9 695 138.3 47.6 .114 1.07 710 56.4 52.7 .124 0.8 690 45.2 56.5 .133 3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 <td< td=""><td>2.5</td><td>595</td><td>3.0</td><td>1.2</td><td>Blank</td></td<>	2.5	595	3.0	1.2	Blank
3.17 575 34.8 11.0 .024 2.0 625 48.1 24.0 .056 1.5 665 47.6 31.7 .074 2.9 695 138.3 47.6 .114 1.07 710 56.4 52.7 .124 0.8 690 45.2 56.5 .133 3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	1.0	580	16.1	16.1	0.036
2.0 625 48.1 24.0 .056 1.5 665 47.6 31.7 .074 2.9 695 138.3 47.6 .114 1.07 710 56.4 52.7 .124 0.8 690 45.2 56.5 .133 3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	0.7	580	9.3	13.3	.029
1.5 665 47.6 31.7 .074 2.9 695 138.3 47.6 .114 1.07 710 56.4 52.7 .124 0.8 690 45.2 56.5 .133 3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	3.17	575	34.8	11.0	.024
2.9 695 138.3 47.6 .114 1.07 710 56.4 52.7 .124 0.8 690 45.2 56.5 .133 3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	2.0	625	48.1	24.0	.056
1.07 710 56.4 52.7 .124 0.8 690 45.2 56.5 .133 3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	1.5	665	47.6	31.7	.074
0.8 690 45.2 56.5 .133 3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	2.9	695	138.3	47.6	.114
3.0 403 8.4 2.8 .004 3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	1.07	710	56.4	52.7	.124
3.0 405 7.4 2.5 .004 1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	0.8	690	45.2	56.5	. 133
1.5 450 6.2 4.1 .007 1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	3.0	403	8.4	2.8	.004
1.5 452 6.3 4.2 .008 1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	3.0	405	7.4	2.5	.004
1.6 487 10.5 8.6 .018 1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	1.5	450	6.2	4.1	.007
1.6 527 15.0 9.4 .020 2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	1.5	452	6.3	4.2	.008
2.0 600 38.6 19.3 .044 1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	1.6	487	10.5	8.6	.018
1.0 637 25.6 25.6 .060 1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	1.6	527	15.0	9.4	.020
1.5 700 81.3 54.0 .128 3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	2.0	600	38.6	19.3	.044
3.9 745 250.7 64.4 .153 2.0 570 2.8 1.4 Blank	1.0	637	25.6	25.6	.060
2.0 570 2.8 1.4 Blank	1.5	700	81.3	54.0	.128
	3.9	745	250.7	64.4	.153
2.9 570 3.6 1.2 Blank	2.0	570	2.8	1.4	Blank
	2.9	570	3.6	1.2	Blank

Average blank, 1.0 mg. of water per hour.

results obtained, selected impartially from a much larger number of determinations, are given in Table V. Here again a rapidly increasing rate of diffusion with increasing temperature is evident, as shown graphically in Fig. 2. The curves here given for copper and nickel have the same general appearance as those obtained by other workers^{6,8,9} for palladium, platinum and rubber. The specific diffusion rate of hydrogen through nickel may be calculated to be about 0.100 at 750° and about 0.012 at 500°. Thus, hydrogen diffuses through nickel at temperatures around 750° about four times as fast as it does through copper, and 80 to 100 times as fast as it does through lead and zinc at temperatures just below the melting points of the latter metals.

Summary

An apparatus has been described for studying the rate of diffusion of gases through definitely measurable areas of sheet metal at definite, uniform temperatures. The specific diffusion rate of hydrogen through several common metals, expressed in milligrams per hour per square centimeter area per millimeter thickness has been found to be:

Metal	Specific diffusion rate	°C.	Metal	Specific	diffusion rate	°C.
Aluminun	1 Not detectable ^a	555	Copper	(0.028	770
Zinc	0.0012	375	Nickel		.012	500
Lead	001	265	Nickel		.100	750
Copper	011	500				

^a Namely, less than about 0.0005.

In addition, the specific diffusion rate of hydrogen through copper and through nickel has been determined over a considerable range of temperature, and the results have been shown graphically.

Further work is in progress, by the junior author, extending this investigation over a wider range of temperature, metal-thickness and pressure variation.

LINCOLN, NEBRASKA

[Contribution from the Chemical Laboratory of the University of California]

THE ACTIVITIES OF ZINC, CADMIUM, TIN, LEAD AND BISMUTH IN THEIR BINARY LIQUID MIXTURES¹

By Nelson W. Taylor Received August 31, 1923

Introduction

The experimental investigations of Tammann, Mever, Ramsay, Richards and co-workers, Hulett and De Lury, Hildebrand and co-workers2 on metallic solutions have been made with the object of discovering whether the simple laws of non-metallic solutions of low polarity were applicable or whether the existence of free electrons in the metals affected their thermodynamic properties. Although the deviations from the simple concentration laws have been found to be great in many cases, it appears that all systems investigated do approach this law asymptotically in dilute solutions. The dissolved molecules are believed to be monatomic and departures from the laws of the ideal solution are to be ascribed to causes other than polymerization or dissociation of the atoms into ions and free electrons. When definite compounds are known to exist in the solid state, it is easy to explain abnormally low fugacities of the components of the solution on the basis of compound formation; but there are a number of cases where the fugacities are much greater than the simple concentration law would require. This type, also very common to organic liquid mixtures, has been suggested by Hildebrand to be due to differences in the internal pressures of the components. This theory has been very well substantiated by a large amount of vapor pressure and solubility data, and by measurements on the critical mixing temperatures of two-phase liquid systems in cases where the relative internal pressures of the components are known. In the field of metallic solutions, however, experimental work has been entirely confined to amalgams and it is of interest to extend our knowledge to other liquid mixtures. In the present investigation, by working above 400°, it has been found possible to obtain accurate values for the activities of both components of the following liquid systems, zinccadmium, zinc-tin, cadmium-tin, cadmium-lead and cadmium-bismuth, over the complete concentration range.

¹ Submitted by the author in partial fulfilment of the requirments for the Degree of Doctor of Philosophy at the University of California, May, 1923.

² (a) Tammann, Z. physik. Chem., 3, 441 (1889). (b) Meyer, Wied. Ann., 40, 244 (1890). (c) Ramsay, J. Chem. Soc., 55, 521 (1889). (d) Hulett and De Lury, This Journal, 30, 1805 (1908). Richards and co-workers, (e) Proc. Am. Acad. Arts Sci., 34, 87 (1898); (f) Carnegie Inst. Pub., 118 (1909); (g) This Journal, 41, 1732 (1919); (h) 44, 60 (1922). (i) Hildebrand, Trans. Am. Electrochem. Soc., 22, 319 (1912); (j) 22, 335 (1912); (k) This Journal, 35, 501 (1913). (l) Hildebrand and Eastman, ibid., 36, 2020 (1914); (m) 37, 2452 (1915). (n) Hildebrand, Foster and Beebe, ibid., 42, 545 (1920).

There are two reliable methods available for investigating the activities of the individual components of liquid metal systems: first, measurements of vapor pressures at high temperatures, as exemplified by the work of Hildebrand and Eastman on silver, gold, bismuth and thallium amalgams; and second, measurements of the electromotive force of concentration cells, in which one electrode consists of a pure metal or an alloy in which this metal has a known activity. The second method has been applied by Richards and his co-workers to a large number of solutions of electropositive metals in mercury. Except in the case of thallium amalgams, the concentration range investigated never exceeded 10% in the electromotive-force measurements but was limited by the low solubility of most of the metals in mercury at room temperature. This method has the theoretical advantage that it measures the activity directly and does not involve the assumption that the vapor obeys the simple gas laws. It has the practical advantage that a number of alloys of different concentrations can be studied simultaneously, and considerable time may be saved. Further, it is possible to work with metals of low vapor pressure. For example, at 500° the vapor pressure of zinc is about 1 mm., which would make accurate measurements somewhat difficult for alloys of low zinc content. Such alloys offer no special difficulty when the electromotiveforce method is applied. Finally, measurements may be readily made over a wide temperature range with none of the difficulties which usually attend vapor pressure work at very high or very low pressures.

In this research the electromotive-force method was used. The ordinary aqueous electrolyte used by Richards was replaced by a fused-salt mixture which contained the ion of the more electropositive component of the binary alloy under investigation. All alloys were measured against the pure electropositive metal. Thus in the system, zinc-tin, the cell may be represented as Zn | Zn++ | Zn-Sn alloy. The reaction taking place when the circuit is closed consists in a transfer of zinc from the pure state at unit activity, to the alloy where the activity of the zinc is a smaller value, a_1 . The electromotive force of such a cell is given by the equation, E = RT/nF $\ln 1/a_1$, where the symbols R, T, n and F have the usual significance. Throughout this article, the symbols a_1 and N_1 will be used to represent the activity and the mole fraction of the more electropositive component of the alloy. Thus from measurements of the electromotive force, the value of the activity may be readily calculated. It is obvious that the above reaction must be the only one taking place in the cell. The electrolyte must contain nothing which might react with either component of the alloy. It is, therefore, essential that the normal electrode potentials of the two components be sufficiently different that the more noble metal will have no effect on the ion of the other. This requirement limits our choice of metal pairs very considerably. The low-melting metals suitable

for this research have the following molal electrode potentials in aqueous solution at 25°. These values can give only a rough indication of the electrode potential of the metals against their fused salts.

Metal	Zinc	Cadmium	Thallium	Tin	Lead	Bismuth
M. p., °C	419	320	302	232	327	269
Elec. pot., volts	0.76	0.40	0.34	0.14	0.12	-0.3

Excluding systems which form two liquid phases and those in which the difference between the electrode potentials is less than 0.20 volt, we are limited to the following cases: Zn-Cd, Zn-Sn, Cd-Sn, Cd-Pb, Cd-Bi, Tl-Sn, Tl-Pb, Tl-Bi. The first five of these systems have been investigated in the present research. It may be of interest to note that some preliminary experiments showed that at 500° in a fused-salt electrolyte the cadmium ion was largely reduced by thallium, which indicates that the thallium has very probably the higher electrode potential at this temperature.

When pure molten zinc chloride or cadmium chloride is used as the electrolyte, metallic fogs are formed.³ When these fogs occur in an alloy concentration cell there results a transfer of metal through the electrolyte until all the alloys have reached the same composition. Reproducible electromotive forces are therefore not obtainable. This difficulty was overcome by using as the electrolyte a eutectic mixture of 40% potassium chloride and 60% lithium chloride which contained a little zinc chloride (or cadmium chloride). This fused-salt mixture shows no tendency to fog formation with any of the alloys investigated. It should perhaps be mentioned that the concentration of zinc or cadmium ion has no effect on the electromotive force of the type of cell used in the present research.

Purity of Materials

The potassium and lithium chlorides used in this research were found to be entirely free from heavy metals. The cadmium and zinc chlorides and potassium hydroxide contained very slight traces of iron, just sufficient to give a faint pink color with potassium thiocyanate. This corresponds to about 0.005% of ferric ion, which is entirely too small to make any appreciable change in the composition of the alloys. These salts contained some water so that there was some hydrolysis on fusion, with the liberation of hydrogen chloride which was neutralized by addition of fused potassium hydroxide.

The cadmium and bismuth had been obtained from a foreign commercial source. Those metals were used without further purification. The presence of 0.5% of impurity would not affect the electromotive force of the cells more than 0.00015 volt, which was the accuracy obtained in the actual measurements. The zinc, tin and lead had been used in a previous investigation in this Laboratory, and were of known purity.

Description of Apparatus

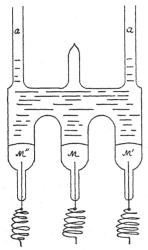
The cell used was a modification of the type used by Richards and Daniels in their study of the electromotive forces of thallium amalgams.^{2g} Since the work was all at high temperatures, Pyrex glass was used. The cell contained 6 cups, in 2 of which were

⁸ Lorentz, Z. anorg. Chem., 91, 46 (1915).

⁴ Hogness, This Journal, 43, 1621 (1921).

placed samples of the more electropositive metal while the other 4 cups contained alloys of known composition. These cups were approximately 12 mm. in internal diameter and 25 mm, in depth. Tungsten wires, sealed through the base of each cup, formed the electrodes. These were soldered with german silver to heavy copper wires which led out of the furnace and connected with the potentiometer. In the first experiments graphite electrodes were used, but this method was soon discontinued on account of the formation of metal carbides. During the course of the research there was no evidence of solution of tungsten in the molten alloys. The cell was supported in the furnace by the long glass tubes, a, Fig. 1. For suggestions in the design of all cells used in this research and for their construction the author is indebted to Mr. W. J. Cummings, glass blower of this Laboratory.

All measurements were made in a large, thick-walled electric furnace which was heated by 4 Nichrome units in parallel. The air inside was circulated by two large fans. By adjustments of current at half-hour intervals the temperature would remain at 580 ± 1.5° with a power input of 2.6 kilowatts. Four temperatures were used: 430°, 475°,



allovs

540° and 580°. The temperatures were measured by means of 2 Chromel-alumel thermocouples which had been calibrated at the melting points of tin, zinc and antimony. The melting points of these metals had been previously determined by means of a platinum-resistance thermometer whose equation was accurately known. The values obtained in the calibration of the thermocouples were plotted on large cross-section paper and smooth curves drawn through them. From these curves all temperatures were obtained by interpolation. The accuracy was about 2°.

Experimental Procedure

Small sticks of the various pure metals were prepared by melting larger pieces in a vacuum and running the molten metal into glass tubes. When the glass was broken the stick came out with a clean surface. Alloys of known compo-Fig. 1.—View of one-half sition were prepared by weighing these sticks. of the 6-cup Pyrex cell. M is The average weight of the whole alloy was 7 or a pure metal, M' and M" are 8 g. These weighed sticks of pure metal were put into the proper cups in the cell, all but two

inlet tubes were sealed off, and the cell was placed in the furnace and heated in a stream of pure hydrogen until the sticks of pure metal had melted and run together to form a more or less homogeneous alloy. In the meantime the electrolyte was prepared by fusion of the eutectic mixture of potassium and lithium chlorides with a small amount of zinc or cadmium chloride and potassium hydroxide. A stick of pure metallic zinc (or cadmium) was usually added to the electrolyte to ensure complete removal of hydrogen When the metals in the cell were melted, the hydrogen flow was stopped and immediately the clear electrolyte was poured into the cell, and care was taken that the globule of zinc (or cadmium) was left behind. Sometimes the electrolyte contained small amounts of zinc oxide or cadmium oxide. This apparently did not affect the electromotive forces obtained.

The heavy copper wires from the cell connected through mercury cups to the potentiometer. This was a commercial instrument and was used in connection with a working battery of 2 Edison accumulators. A Weston cell, giving an electromotive force of 1.01862 volts at 22° was used as standard. This cell was frequently checked against other standard cells in this Laboratory, and was found to remain constant.

Using a 6-cup cell, in which 2 cups contain the same pure metal, it is possible to make duplicate measurements of the electromotive forces of the pure metals against each of the 4 alloys. These electromotive forces may be checked further by measurements of various combinations of the alloys themselves and by suitable additions and subtractions of the values obtained. The alloys at first were not homogeneous so that the electromotive forces changed more or less rapidly at first, but after 5 or 6 hours, they became constant to 0.1 mv. and remained so during the subsequent 3 days. Temperature readings and electromotive-force readings were taken every half hour until 10 or 12 readings had been obtained and it was evident that the electromotive forces were remaining constant.

The furnace temperatures were usually changed in the following order: 470°, 540°, 470°, 430°, 540°, 580° and 470°. The advantage of returning to a previous temperature after 8 or 10 hours is that the old electromotive forces may be thus checked to see whether they have remained constant over long periods of time. Any change which might take place in the composition of the alloys is thus readily detected. In some cases the electromotive forces were found to have risen 0.2 or 0.3 mv. over a 24-hour period. This was apparently due to a very slow diffusion of oxygen through the electrolyte to the alloy surfaces. In cases where the electromotive forces had changed in this way, all subsequent measurements were corrected by the amount of the change. All final electromotive force values are averages of 10 or more readings. The duration of a complete run was ordinarily 50 to 60 hours, but there were a number of cases where leaks developed and the run was not completed. The fused electrolyte has a devitrifying action on Pyrex glass so that the cell usually became quite fragile after 2 or 3 days' heating and it was necessary to build a new cell for every run.

To illustrate the constancy of the electromotive-force values over a long period of time, the following data are quoted from the system, cadmiumlead (Run 3). The time is measured from the beginning of the run.

The experimental results on the various alloy systems will now be recorded, together with the values of $\log (a/N)$ calculated from the actual data. The significance of the quantity $\log (a/N)$ may be made clearer by considering the following relationships. In general, when 1 mole of one

component is transferred from the pure state to an alloy in which its activity is a_1 the decrease of free energy is $\Delta F = RT \ln a_1$. If the liquid

Table I

Summary of Typical Run

Electromotive force of Cd concentration cells in Cd-Pb alloys, Run 3

Average of readings	Cell 15	Cell 14	Cell 13	- Cell 12	Temper ature °C.	Thermo- couple	Hours
15	0.0355	0.0181	0.0097	0.0060	476	0.01291	0-12
6	.0353	.0174	.0099	.0056	474	.01279	30-35
2	.0347		.0097	.0061	475	.01282	57-58
Weighted mean	.0355	.0181	.0097	.0060	476	.01290	
4	.0307	.0154	.0080	.0054	427	.01137	12-15
10	.0306	.0154	.0082	.0054	428	.01140	24 - 29
Weighted mean	.0307	.0154	.0081	.0054	427	.01138	
6	.0424	.0225	.0122	.0074	544	.01515	35-38
4	.0422	.0226	.0122	.0073	545	.01518	48 - 50
Weighted mean	.0424	.0225	.0122	.0074	544	.01516	
10	.0450	.0244	.01315	.0078	572	.01610	51 - 56

alloy obeys Raoult's law the free energy decrease is $\Delta F = RT \ln N_1$. The excess free energy of one component of an actual alloy over the value which it would have if the solution were ideal, is $\Delta F = RT \ln (a_1/N_1)$. Furthermore, since a/N is equal to unity for an ideal solution, a curve of a_1/N_1 or $\log (a_1/N_1)$ plotted against N_1 makes a very satisfactory way of representing the deviation of any solution from the ideal. The horizontal line corresponding to $\log (a/N) = 0$ represents Raoult's law. By extrapolating the $\log (a_1/N_1)$ curve to the point where N_1 is equal to zero it is easy to obtain the limiting value of a_1/N_1 , which is the so-called Henry's-law constant for this component. As a matter of fact, the curves exhibited in this article show that a_1/N_1 is never constant over any finite range of concentration, and therefore the Henry's-law constant cannot really be considered a constant at all, although in a great deal of vapor-pressure data recorded in the literature this ratio has been found "constant" within fairly narrow limits of experimental error.

The activity of the second component of these alloys has been obtained from that of the first by means of the Duhem equation, which may be expressed as follows: N_2 d log $(a_2/N_2) = -N_1$ d log (a_1/N_1) . This may be written in the integrated form $\log (a_2/N_2) = -\int_0^{N_2} N_1/N_2$ d log (a_1/N_1) .

The value of the right-hand term of this expression may be determined by first deriving an empirical equation which will give the experimental values of $\log (a_1/N_1)$ as a function of N_1 , and then carrying out the above integration. In the present research it was found simpler, however, to plot the smoothed-out values of $\log (a_1/N_1)$ at even mole fractions as abscissas against the corresponding values of N_1/N_2 as ordinates, and to determine

the area under the curve up to any desired value of N_2 . This process, although somewhat tedious, may be carried out with a fairly high degree of accuracy and rapidity. There are two choices of a standard state for the second component of the alloy. The standard state of the first component has been fixed by defining $a_1=1$ when $N_1=1$. The same choice is made in this article for the second component, namely $a_2=1$ when $N_2=1$. The other possibility is to define a_2/N_2 as equal to unity when $N_2=0$. The two standard states are related by a constant factor. For example, in cadmium-tin solutions at 483° , the value of $a_2/N_2=2.15$ when $N_2=0$. If the value of a_2/N_2 when $N_2=0$ had been defined as equal to unity, all the other values for a_2/N_2 in the other concentrations would be obtained by dividing the present values by 2.15.

The System: Cadmium-Tin

Four runs were made, two of which were successful. The following values are the actual electromotive forces obtained. Each value is the average of about 10 readings taken at half-hour periods. In this and in

TABLE II
THE SYSTEM: CADMIUM-TIN

	Run 2		
n of alloy	No. 2	No. 3 No. 4	No. 5
, -,			0.0835
Electi	romotive force	e in volts	
Cell 12	13	14	15
0.0051	0.0129	0.0292	0.0578
.0053	.0141	.0324	.0632
.0061	.0161	.0368	.0707
.0064	.0173	.0395	.0749
ulated values o	$f \log(a_1/N_1)$ fr	rom these measurem	ents
Alloy No. 2	No. 3	No. 4	No. 5
0.015	0.060	0.170	0.250
.018	.057	.157	.236
.013	.047	.135	.207
.013	.042	.124	.198
	Run 4		
on of alloy on Cd (N_1)	No. 2 0.749	No. 3 No. 4 0.630 0.451	No. 5 0.222
Elec	tromotive for	ce in volts	
Cell 12	13	14	15
0.0071	0.0099	0.0166	0.0315
.0077	.0111	.0185	.0355
.0085	.0126	.0213	.0406
lculated values	of $\log(a_1/N_1)$	from these measure	ments
Alloy No. 2	No. 3	No. 4	No. 5
0.024	0.059	0.108	0.203
.023	.053	.099	.180
.021	.045	.083	.152
	on Cd (N_1) Elect: Cell 12 0.0051 .0053 .0061 .0064 ulated values of Alloy No. 2 0.015 .018 .013 .013 on of alloy fon Cd (N_1) Elect: Cell 12 0.0071 .0077 .0085 lculated values Alloy No. 2 0.024 .023	n of alloy No. 2 on Cd (N_1) 0.816 Electromotive force Cell 12 13 0.0051 0.0129 .0053 .0141 .0061 .0161 .0161 .0064 .0173 ulated values of $\log(a_1/N_1)$ for Alloy No. 2 No. 3 0.015 0.060 .018 .057 .013 .047 .013 .042 Run 4 on of alloy No. 2 Run 4 on of alloy No. 2 Run 4 on Cd (N_1) 0.749 Electromotive for Cell 12 13 0.0071 0.0099 .0077 .0111 .0085 .0126 lculated values of $\log(a_1/N_1)$ Alloy No. 2 No. 3 0.024 0.059 .023 .053	n of alloy No. 2 No. 3 No. 4 on Cd (N_1) 0.816 0.569 0.258 Electromotive force in volts Cell 12 13 14 0.0051 0.0129 0.0292 .0053 .0141 .0324 .0061 .0161 .0368 .0064 .0173 .0395 ulated values of $\log(a_1/N_1)$ from these measurementally No. 2 No. 3 No. 4 0.015 0.060 0.170 .018 .057 .157 .013 .047 .135 .013 .042 .124 Run 4 From of alloy No. 2 No. 3 No. 4 0.00Cd (N_1) 0.749 0.630 0.451 Electromotive force in volts Cell 12 13 14 0.0071 0.0099 0.0166 .0077 .0111 .0185 .0085 .0126 .0213 lculated values of $\log(a_1/N_1)$ from these measurementalloy No. 2 No. 3 No. 4 0.024 0.059 0.108 .023 .053 .099

subsequent tables, the term, "Cell 12," is used to represent a cell of which one electrode was pure cadmium and the other electrode was alloy No. 2.

TABLE III
THE SYSTEM: CADMIUM-TIN

			2			- 1			
		A 431°	•				B 483°		
N_1	$Log(a_1/N_1)$) a1	$\text{Log}(a_2/N_2)$	a 2	$\text{Log}(a_1/N_1)$	a_1	$Log(a_2/N_2)$	a 2	N_2
0.0	0.305	0.000	0.000	1.00	0.279	0.00	0.000	1.00	1.0
.1	.253	.179	.003	0.91	.229	.17	.0027	.91	0.9
.2	.206	.32	.011	.82	.184	.31	.0105	.82	.8
.3	.161	.435	.026	.74	.144	.42	.024	.74	.7
.4	.122	.53	.047	.67	.109	.51	.043	.66	.6
.5	.087	.61	.076	.60	.079	.60	.067	.58	.5
.6	.058	.68	.109	.52	.054	.68	.098	.50	.4
.7	.034	.76	.154	.43	.033	.76	.137	.41	.3
.8	.017	.83	.207	.32	.017	.83	.184	.31	.2
.9	.006	.92	.273	.19	.006	.91	.250	.18	.1
1.0	.000	1.00	.35	.00	.000	1.00	.333	.00	.0
	(C 544°					D 585°		
0.0	0.246	0.00	00000.0	1.00	0.232	0.00	0.0000	1.00	1.0
.1	.200	.16	.0025	0.91	.188	.15	.0023	0.91	0.9
.2	.160	.29	.0095	.82	.148	.28	.0093	.82	.8
.3	.123	.40	.022	.74	.112	.39	.021	.74	.7
.4	.093	.50	.038	.66	.083	.48	.037	.65	.6
.5	.067	.58	.059	.57	.059	.57 ·	.057	.57	.5
.6	.045	.67	.086	.49	.039	.66	.082	.48	.4
.7	.027	.75	.117	.39	.024	.74	.110	.39	.3
.8	.014	.83	.158	.29	.012	.82	.147	.28	.2
.9	.005	.91	.210	.16	.0045	.91	.193	.16	.1
1.0	.000	1.00	.275	.00	.0000	1.00	.25	.00	.0

The calculated values of $\log (a_1/N_1)$ obtained from these two runs have been plotted against N_1 . The average deviation of the individual values from the smooth curves is 0.006 at 433°, 0.004 at 484° and 0.002 at 546°. In determining the curve, equal weight has been given to all the experimental points, but it is possible that the values for Run 2 are somewhat low and that all the values on the curve should be slightly higher. The smoothed-out values of $\log (a_1/N_1)$ and the corresponding calculated values of $\log (a_2/N_2)$ at various mole fractions are recorded in Table III (A–D). The values of a_1 and of a_2 are also given.

Part of the data is summarized further in Fig. 2, and in Fig. 3. The results at all the temperatures are not shown in these curves but are used later in calculating heats of dilution.

The System: Cadmium-Lead

Three complete runs were made on cadmium-lead alloys. The electromotive-force values recorded are each averages of 10 or more individual readings. The average deviation of the individual points from the smooth $\log (a_1/N_1)$ curve is as follows: 0.004 at 432°; 0.002 at 480°; and 0.002 at

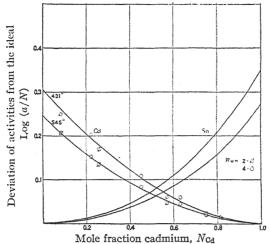


Fig. 2.—System, cadmium-tin. Deviation from the laws of the perfect solution. The horizontal line $\log (a/N) = 0$ corresponds to Raoult's law

 544° ; and 0.001 at 572° . The smoothed-out values of log (a_1/N_1) and the corresponding values for log (a_2/N_2) are recorded in Table V (A–D). Part

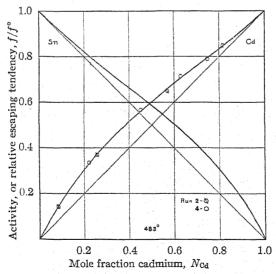


Fig. 3.—Activity curves for the system, cadmium-tin, at 483°

of the data is summarized further in Figs. 4 and 5. Comparison of these with the corresponding curves for cadmium-tin alloys shows about

	TAE	BLE IV
THE	System:	CADMIUM-LEAD
	D.	TTAT 1

		RUN	Ţ							
	on of alloy tion $Cd(N_1)$	No. 2 0.786	No. 3 0.584	No. 4 0.401		No. 5 0.155				
20	Electromotive force in volts									
Temp. °C.	Cell 12	13	1-	4	15					
436	0.0043	0.0073	0.0	108	0.0	274				
484	.0047	.0081		131						
Cal	culated values	of $\log(a_1/N_1)$	from these	measure	ments					
Temp.	Alloy No. 2	No. 3	No	0.4	No.	. 5				
436	0.0441	0.130	0.2	43	0.4	21				
484	.042	.126	.2	23						
		Run	2							
	on of alloy	No. 2	No. 3	No. 4		No. 5				
Mole fract	tion Cd (N_1)	0.696	0.509	0.569	C	1.123				
Electromotive force in volts										
Temp.	Cell 12	13	1	4		15				
427	0.0054	0.0081	0.0	154	0.0	307				
476	.0060	.0097	.0	181	.0	355				
544	.0074	.0122	.0	225	.0	.0424				
572	.0078	.0132	.0	244	.0	450				
Calc	ulated values o	$f \log(a_1/N_1)$	from these:	measuren	nents					
Temp.	Alloy No. 2	No. 3	No	. 4	No.	. 5				
427	0.080	0.176	0.3	49	0.40	69				
476	.077	.163	.3	27	.4	34				
544	.066	.143	.2	93	.3	89				
572	.064	.136	.2	80	.3	75				
		Run 3	3							
	on of alloy ion $Cd(N_1)$	No. 2 0.293								
Electron	notive force in	volts:	544° 0.	0215	466°	0.0170				
Calculat	ed values of lo	$g(a_1/N_1)$	544° 0.	268	466°	0.301				

twice as great departure from Raoult's law as in the case of the system, cadmium-lead. This important fact will be discussed later.

TABLE V
THE SYSTEM: CADMILIM-LEAD

			1 1115	NOIDM.	CADMIUM-1	しだみひ			
		A 432°					B 480°		
N_1	$Log(a_1/N_1)$	aı	$\text{Log}(a_2/N_2)$	a 2	$Log(a_1/N_1)$	aı	$Log(a_2/N_2)$	a_2	N_2
0.0	0.57	0.000	0.0000	1.000	0.55	0.000	0.0000	1.000	1.0
.1	.484	.305	.0047	0.910	.455	.285	.0052	0.910	0.9
.2	.398	.500	.0197	.835	.369	.470	.021	.840	.8
.3	.316	.620	.047	.780	.292	.590	.046	.780	.7
.4	.244	.700	.086	.730	.226	.675	.082	.725	.6
.5	.180	.755	.138	.685	.169	.740	.129	.675	. 5
.6	.125	.800	.204	.640	.119	.790	.190	.620	.4
.7	.078	.840	.292	.585	.075	.830	.272	.560	.3
.8	.040	.875	.406	.510	.038	.875	.383	.485	.2
.9	.013	.925	.560	.365	.012	.925	.539	.345	.1,
1.0	.000	1.000	.80	.000	.000	1.000	.74	.000	.0

		C 544°					D 572°		
		C 944					D 012		
0.0	0.480	0.000	0000.0	1.000	0.463	0.000	0.0000	1.000	1.0
.1	.404	2.55	.0042	0.910	.391	.245	.0039	0.910	0.9
.2	.334	.430	.017	.830	.322	.420	.016	.830	.8
.3	.266	.555	.039	.765	.257	.540	.038	.765	.7
.4	.202	.635	.074	.710	.196	.630	.071	.710	.6
.5	.148	.705	.118	.655	.140	.690	.117	.655	.5
.6	.103	.760	.173	.595	.097	.750	.170	.590	.4
.7	.065	.815	.244	.525	.063	.810	.233	.515	.3
.8	.034	.865	.336	.435	.035	.865	.316	.415	.2
.9	.011	.920	.476	.300	.0105	.920	.464	.290	.1
1.0	.000	1.000	.67	.000	.0000	1.000	.63	.000	.0

The System: Cadmium-Bismuth

Satisfactory measurements were obtained in four different runs. The recorded electromotive-force values are again averages of 10 or more individual readings.

During this run (No. 4) the wire connecting with the pure cadmium electrode broke, and it was impossible to measure Cells 12, 13, etc., directly. Cells 32, 34 and 35 were, therefore, measured and the electro-

Table VI
The System: Cadmium-Bismuth

		Run 3						
	on of alloy ion $Cd(N_1)$	No. 2 0.727	No. 3 0.639	No. 4 0.456	No. 5 0.230			
	Elec	tromotive for	ce in volts	100				
Temp. °C.	Cell 12	13	14		15			
433	0.0090	0.0139	0.02	69	0.0477			
475	.0098	.0154	.02	89	.0513			
534	.0106	.0170	.03		.0562			
Cal	culated values of	of $\log(a_1/N_1)$	from these r	neasureme	ents			
Temp.	Alloy No. 2	No. 3	No. 4		No. 5			
433	0.0100	-0.0051	-0.049	25 -	-0.0423			
475	.0063	0129	04	79 -	0526			
534	.0061	0176	04	70 -	0632			
Run 5								
	on of alloy ion $Cd(N_1)$	No. 2 0.864	No. 3 0.472	No. 4 0.282	No. 5 0.1134			
	Elec	tromotive for	ce in volts					
Temp.	Cell 12	13	14		15			
422	0.0039	0.0257	0.04	16	0.0673			
471	.0040	.0279	.04	46	.0726			
528	.0043	.0305	.05	09	.0789			
Cal	culated values o	of $\log(a_1/N_1)$:	from these r	neasureme	ents			
Temp.	Alloy No. 2	No. 3	No. 4		No. 5			
422	0.0070	-0.0465	-0.05	40	-0.0305			
471	.0095	0521	05	48 -	0379			
528	.0096	0579	09	11 -	0474			

Table VI (Continued)

Run 6										
Compositio		No. 2	No. 3	No. 4 No. 5						
Mole fracti	on Cd (N_1)	0.857	0.605	0.372 0.164						
	Elec	tromotive for	ce in volts							
Temp.	Cell 12	13	14	15						
431	0.0041	0.0161	0.0034	0.0570						
479	.0045	.0175	.0361	.0620						
533	.0051	.0193	.0393	.0673						
577 .0056		.0207	.0420	.0717						
Calo	culated values o	of $\log(a_1/N_1)$	from these me	asurements						
Temp.	Alloy No. 2	No. 3	No. 4	No. 5						
431	0.0086	-0.0119	-0.0483	-0.0298						
479	.0070	— .0159	0540	- .0445						
533	.0035	-0.0227	0620	- .0550						
577	.0009	0270	0680	0640						
Run 4										
Compositio		No. 2	No. 3	No. 4 No. 5						
Mole fract	ion Cd (N_1)	0.859	0.478	0.316 0.127						

motive-force values are recorded here. The electromotive force for Cell 13 has been obtained by assuming that the $\log (a_1/N_1)$ value for Alloy 3 is correctly given by interpolation from the smooth plot of the other $\log (a_1/N_1)$ values obtained from the other runs. Thus for Cell 13, $E = RT/nF [\log (a_1/N_1) + \log N_1]$. The measured values are as follows.

Temp. °C.	Cell 32	34	35	$Log(a_1/N_1)$ for Alloy No. 3
473	-0.0222	0.0146	0.0423	-0.0470
532	0241	.0157	.0457	- .0540

Each electromotive-force value at the lower temperature represents the average of 16 actual readings. They are, therefore, quite reliable. Each of the values at 532° is an average of 7 readings. From these results the following electromotive forces are obtained by the method just described.

Temp. °C.	Cell 12	13	14	15
473	0.0042	0.0264	0.0410	0.0685
532	.0050	.0291	.0448	.0748

The corresponding calculated values for $\log (a_1/N_1)$ are

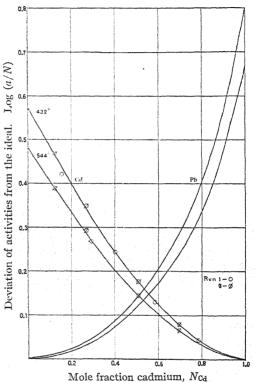
Temp				
Temp. °C.	Alloy No. 2	No. 3	No. 4	No. 5
473	0.0095	-0.047	-0.053	-0.027
532	.0034	054	061	- .039

The point corresponding to Alloy No. 5 is entirely off the $\log (a_1/N_1)$ curve, but the other points from this run fall very close to this curve with an average deviation of 0.0005 at $473\,^{\circ}$ and of 0.004 at $532\,^{\circ}$. When all the points from the 4 runs are examined the average deviation of these points from the accepted smooth curve is found to be 0.002 at $431\,^{\circ}$, 0.001 at $477\,^{\circ}$ and 0.002

at 533°. This is about the magnitude of the effect produced by an uncertainty of 0.1 mv. The activities of the components of the system cadmium-bismuth are, therefore, known with considerable accuracy.

Table VII (A–C) records the interpolated values of log (a_1/N_1) and of log (a_2/N_2) at various mole fractions of cadmium. The results are of great

interest, in that they show the remarkable behavior of cadmium-bisthe system, muth, in deviating to a greater extent from the ideal solution [where log (a_1/N_1) = 0] at high temperatures than 0] at high temperatures than tow. Cases of this kind are very rare. The system, cadmium-bismuth, is evidently very complex. It is possible that some tendency exists to form a weak compound, Cd₃Bi₂, in the liquid state. Such a factor would reduce the activities of both components and would tend 5 to annul the effect of any factor which produces abnormally large activities. When this system was investigated no compound between cadmium and bismuth had been reported in the literature from a study of freezing-point data. At the suggestion of of this Laboratory made a



a study of freezing-point data. At the suggestion of the laws of the perfect solution. The horizontal the author, Mr. H. C. Betts $\log (a/N) = 0$ corresponds to Raoult's law

series of cooling curves on cadmium-bismuth alloys of about the composition corresponding to Cd_3Bi_2 . He discovered at 161° a slight break in the freezing-point curve, which indicates the existence of a weak compound. The existence of this compound is not surprising, since freezing-point diagrams show evidence of compounds corresponding to Zn_3Sb_2 and Cd_3Sb_2 .

The results are further summarized in Figs. 6 and 7. The initially high activity of each component when present in large excess is evidence that at such concentrations the internal pressure difference is the predominating factor. As the mole fractions of the two components become more nearly

equal, their activities are abnormally reduced by formation of compounds in solution. The Duhem relation requires that when the log (a_1/N_1)

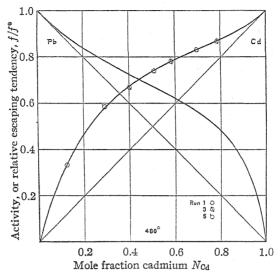


Fig. 5.—Activity curves for the system, cadmium-lead at 480°

curve shows a minimum there will be a corresponding maximum for the log (a_2/N_2) curve at the same composition. This is well brought out in Fig. 6. Similarly, when one curve shows a point of inflection the other must

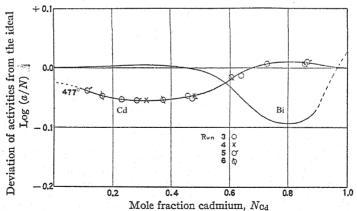


Fig. 6.—System, cadmium-bismuth. Deviation from the laws of the perfect solution. The horizontal line $\log (a/N) = 0$ corresponds to Raoult's law

also change its curvature. In Fig. 6 the log (a_2/N_2) curve (for bismuth) inflects at about $N_{\rm Cd}=0.15$. Hence, the log (a_1/N_1) curve (for cadmium) has been drawn with an inflection at the same point, although unfortu-

TABLE VII
THE SYSTEM: CADMIUM-BISMUTH

		1	HE SYSTEM: CA	dmium-Bismuti	HI.		
		A 431°			B 477	•	
N_1	$\text{Log}(a_1/N_1)$		$\log(a_2/N_2)$ a_2	$\text{Log}(a_1/N_1)$	$a_1 = \text{Log}(a_2/N)$	2) a2	N_2
0.0	-0.010	0.000 (0.0000 1.000	-0.024 0.0	0.000	1.000	1.0
.1	025	.095	.0008 0.902	- .036 .0	0006	0.902	0.9
.2	039	.183	.0033 .806	- .050 .:	178 .0031	.806	.8
.3	- .048	.269	.0063 .710	055 .5	264 .0046	.708	.7
.4	048	.358	.0062 .609	- .053 .:	354 .0034	.605	.6
.5	- .039	.457 —	.0013 .498	- .044 .4	452 - .0043	.495	.5
.6	— .014	.581 —	.0300 .373	021 .3	572033	.371	.4
.7	+ .008	.714 -	.0690 .256	+ .004 .7	707078	.251	.3
.8	+ .0106	.82 —	.0760 .168	+ .010 .8	818 — .095	.161	.2
.9	+ .006	.913 —	.046 .090	+ .006 .	912070	.085	.1
1.0	+ .000	1.000 +	.12 .000	+ .000 1.0	000 + .024	.000	.0
			C 5	33°			
	N_1	$\text{Log}(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	N_2	
	0.0	-0.030	0.000	0.0000	1.000	1.0	
	.1	— .046	.090	.0008	0.902	0.9	
	.2	- .060	.174	.0033	.806	.8	
	.3	- .064	.259	.0044	.707	.7	
	.4	061	.348	.0028	.604	.6	
	.5	052	.444	0050	.495	.5	
	.6	- .028	.563	035	.369	.4	
	.7	+ .002	.704	- .091	.243	.3	
	.8	+ .0085	.816	- .110	.155	.2	
	.9	+ .0055	.912	- .091	.081	.1	
	1.0	+ .000	1.000	+ .010	.000	.0	

nately no experimental point was obtained at concentrations of cadmium less than $N_{\mathrm{Cd}}=0.1$.

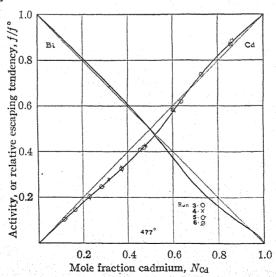


Fig. 7.—Activity curves for the system, cadmium-bismuth at 477°

The System: Zinc-Cadmium

Three independent runs were made on zinc-cadmium alloys and reliable electromotive-force measurements were obtained at 435° , 466° and 540° . The data follow. Each electromotive-force value is the average of 10 or more readings.

TABLE VIII
THE SYSTEM: ZINC-CADMIUM

D 7737 1

		Run 1					
	on of alloy zion Zn (N_1)	No. 2 0.786	No. 3 0.602	No. 4 0.373	No. 5 0.244		
***	Ele	etromotive for	rce in volts				
Temp. °C.	Cell 12	13	14		15		
469	0.0037	0.0069	0.0	125	0.0237		
539	.0042	.0080	.0	153	.0291		
Cal	culated values	of log (a_1/N_1)	from these	measurem	ients		
Temp.	Alloy No. 2	No. 3	No.		No. 5		
469	0.054	0.127	0.2	59	0.291		
539	.052	.121	.23	38 .	.251		
		Run 2					
	on of alloy	No. 2	No. 3	No. 4	No. 5		
Mole fract	tion $Zn(N_I)$	0.150	0.344	0.536	0.690		
		ctromotive for	ce in volts				
Temp.	Cell 12	13	14		15		
436	0.0275	0.0136	0.00	083	0.0058		
464	.0294	.0147	.00	084	.0063		
541	.0367	.0182	.0.	105	.0068		
572	.0396	.0200	.0:	126	.0080		
Cal	culated values	of $\log(a_1/N_1)$	from these	measurem	ents		
Temp.	Alloy No. 2	No. 3	No	. 4	No. 5		
436	0.432	0.271	0.1	53	0.0786		
464	.421	.263	.1	56	.0750		
541	.368	.239	.14	11	.0769		
572	.351	.225	.13	21.	.0657		
		Run 3					
	on of alloy	No. 2	No. 3	No. 4	No. 5		
Mole fract	ion Zn (\tilde{N}_1)	0.848	0.687	0.456	0.251		
		ctromotive for	ce in volts				
Temp.	Cell 12	13	14		15		
434	0.0021	0.0047			0.0170		
464	.0024	.0052	0.0	129	.0186		
541	.0031	.0067	• •	• •	.0235		
Cal	culated values	of $\log(a_1/N_1)$:	from these	measurem	ents		
Temp.	Alloy No. 2	No. 3	No.	4	No. 5		
434	0.0422	0.0958			0.359		
464	.0385	.0910	0.16	34	.347		
541	.0333	.0798			.310		

These log (a_1/N_1) values have been plotted against N_1 and smooth curves obtained. The average deviation of the experimental points

from the accepted curves is 0.004 at 435° , 0.003 at 466° and 0.003 at 540° . These correspond to an average accuracy of 0.2 mv.

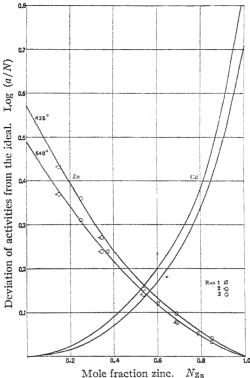


Fig. 8.—System, zinc-cadmium. Deviation from the laws of the perfect solution. The horizontal line $\log (a/N) = 0$ corresponds to Raoult's law

The smoothed-out values at even mole fractions are recorded in Table IX (A-C). The $\log a/N$ data for 540° and for 435° are further summarized in

Table IX The System: Zinc-Cadmiu

			THEOX	STEM: Z	INC-CADMIU	M			
		A 435°)				B 466°		
N_1	$Log(a_1/N_1)$	a_1	$\text{Log}(a_2/N_2)$	a_2	$Log(a_1/N_1)$	aı	$Log(a_2/N_2)$	<i>a</i> 2	N_2
0.0	0.57	000.0	0.0000	1.000	0.55	0.000	0.000	1.000	1.0
.1	.482	.303	.0040	0.909	.46	.288	.005	0.910	0.9
.2	.395	.497	.0205	.838	.383	.483	.019	.835	.8
.3	.311	.615	.050	.784	.302	.600	.046	.780	.7
.4	.240	.695	.089	.740	.233	.684	.083	.725	.6
.5	.181	.758	.138	.685	.176	.750	.130	.675	.5
.6	.131	.811	.199	.635	.127	.805	.190	.620	.4
.7	.092	.865	.272	.560	,087	.855	.265	.550	.3
.8	.056	.910	.382	.48	.052	.900	.370	.470	.2
.9	.025	.950	.561	.365	.020	.945	.54	.35	.1
1.0	.000	1.000	.84	.000	.000	1.000	.80	.000	.0

		TABLE IX	(Continued)		
		C	540°		
N_1	$Log(a_1/N_1)$	a1	$Log(a_2/N_2)$	a ₂	N_2
0.0	0.490	0.000	0.000	1.000	1.0
.1	.413	.260	.004	0.910	0.9
.2	.340	.440	.017	.830	.8
.3	.274	.565	.039	.765	.7
.4	.216	.660	.070	.705	.6
.5	.163	.730	.113	.650	.5
.6	.117	.785	.169	.590	.4
.7	.079	.840	.242	.525	.3
.8	.046	.890	.341	.440	.2
.9	.018	.940	.50	.32	.1
1.0	.000	1.000	.71	.00	.0

Fig. 8, while the activities of each component at 466° are plotted against the mole fraction of zinc in Fig. 9.

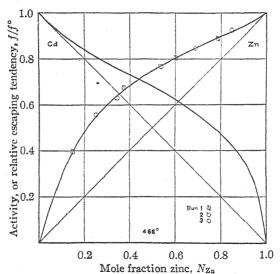


Fig. 9.—Activity curves for the system, zinc-cadmium at 466°

The System: Zinc-Tin

Three independent runs have been made on alloys of zinc with tin, and reliable results have been obtained at 431°, 466°, 539° and 570°. The data follow. Each electromotive-force value is the average of 10 or more readings.

When these $\log (a_1/N_1)$ values are plotted against N_1 the points from Run 2 are found to fall uniformly lower than the points from the other two runs. This was to be expected, since in preparing the electrolyte for Run 2 no potassium hydroxide was added to neutralize the hydrogen chloride

liberated by hydrolysis of the fused chlorides. When the electrolyte was poured into the cell a small evolution of hydrogen took place. Since the zinc in these alloys would be preferentially oxidized by the hydrogen ion in the electrolyte, its mole fraction in the alloys would be reduced, the elec-

TABLE X
THE SYSTEM: ZINC-TIN

		Run 1			
	ion of alloy tion $\operatorname{Zn}\ (N_1)$	No. 2 0.845	No. 3 0.583	No. 4 0.384	No. 5 0.221
i va	Elec	ctromotive for	ce in volts		
Temp. °C.	Cell 12	13	1	1	15
431	0.0024	0.0065	0.0	138	0.0267
466	.0026	.0078	.0	161	.0303
537	.0035	.0104	.0:	205	.0369
570	.0038	.0106	.0:	226	.0401
Ca	lculated values	of $\log(a_1/N_1)$	from these	measurem	ents
Temp.	Alloy No. 2	No. 3		o. 4	No. 5
431	0.0389	0.1409	0.2	183	0.2734
466	.0385	.1280	.1	965	.2430
537	.0298	.1045		605	.1960
570	.0280	.0955	.1	455	.1765
		Run 2			
Compositi	ion of alloy	No. 2	No. 3	No. 4	No. 5
	tion Zn (N_1)	0.142	0.310	0.473	0.721
	Elec	ctromotive for	ce in volts		
Temp.	Cell 12	13	1	4	15
467	0.0436	0.0220	0.0	123	0.0050
537	.0523	.0276	.0	161	.0068
Ca	lculated values	of $\log(a_1/N_1)$	from these	measurem	ents
Temp.	Alloy No. 2	No. 3	No	. 4	No. 5
467	0.253	0.209	0.1	57	0.074
537	.197	.165	.1	25	.058
		Run 3			
	ion of alloy	No. 2	No. 3	No. 4	No. 5
Mole frac	tion $Z_{n}(N_{1})$	0.173	0.497	0.644	0.780
		etromotive for			
Temp.	Cell 12	13		4	15
432	0.0327	0.0088	0.0		0.0029
467	.0364	.0102		061	.0035
541	.0443	.0135		078	.0045
Cal	lculated values		from these	measurem	ents
Temp.	Alloy No. 2	No. 3	No.	4	No. 5
432	0.294	0.178	0.1	20	0.067
467	.266	.165	.10		.060
541	.213	.137	.0	95	.052

tromotive forces obtained would be too high and the calculated values of $\log (a_1/N_1)$ would be too low. When these $\log (a_1/N_1)$ values from Run 2 are corrected by adding a constant factor of 0.010 at 466° and of 0.012

at 539° they fall very closely upon the smooth curve obtained from the data of the other two runs. The average deviation of all the experimental points from the accepted curve then becomes 0.001 at 431°, 0.001 at 466°, 0.003 at 539° and 0.000 at 570°.

The smoothed-out values of $\log (a_1/N_1)$ and the corresponding values of $\log (a_2/N_2)$ calculated by the Duhem relation are recorded in Table XI (A–D). Figs. 10 and 11 also summarize part of these data. The values from Run 2 are not shown in the plots.

TABLE XI
THE SYSTEM: ZINC-TIN

				~ 62624					
		A 431	•				B 466°		
N_1	$\text{Log}(a_1/N_1)$	a 1	$\text{Log}(a_2/N_2)$	a_2	$Log(a_1/N_1)$	a1	$\text{Log}(a_2/N_2)$	a_2	N_2
0.0	0.339	0.000	0.0000	1.000	0.302	0.000	0.0000	1.000	1.0
.1	.310	.204	.0016	0.904	.276	.189	.0014	0.903	0.9
2	.280	.380	.007	.815	.249	.355	.0062	.810	.8
.3	.248	.530	.018	.730	.220	.500	.015	.725	.7
.4	.213	.655	.037	.655	.192	.620	.032	.645	.6
.5	.176	.750	.068	.585	.160	.725	.058	.570	.5
.6	.136	.821	.117	.524	.124	.800	.102	.505	.4
.7	.097	.875	.191	.465	.088	.860	.170	.445	.3
.8	.058	.914	.308	.405	.053	.905	.274	.375	.2
.9	.024	.950	.506	.320	.022	.945	.459	.290	.1
1.0	.000	1.000	.76	.000	.000	1.000	.72	.000	.0
		C 539°	ı				D 570°		
0.0	0.240	0.000	0.0000	1.000	0.212	0.000	0.0000	1.000	1.0
.1	.221	.165	.0010	0.902	0.196	.157	.0008	0.902	0.9
.2	.202	.318	.0044	.808	.180	.303	.0037	.806	.8
.3	.181	.455	.011	.720	.162	.435	.010	.720	.7
.4	.158	.575	.024	.635	.142	.555	.021	.630	.6
5	.132	.680	.045	. 555	.117	.655	.041	.550	.5
.6	.103	.760	.080	.480	.090	.740	.074	.475	.4
.7	.073	.830	.136	.410	.062	.810	.127	.402	.3
.8	.0445	.885	.222	.333	.038	.875	.198	.315	.2
.9	.0185	.940	.379	.240	.016	.935	.325	.210	.1
1.0	.000	1.000	.60	.000	.000	1.000	.54	.000	.0

The form of the $\log (a_1/N_1)$ curve for zinc in these alloys differs somewhat from that shown by the components of cadmium-tin, cadmium-lead, cadmium-zinc alloys. For these the $\log (a/N)$ curves are approximately though not exactly represented by a half-parabola, whereas for zinc in zinc-tin alloys the $\log (a_1/N_1)$ curve flattens out considerably in all alloys containing less than about 60% zinc. The limiting value of $\log (a_1/N_1)$ where $N_1=0$, is about one-half what it would be if the curve had remained parabolic over the whole range. The activity coefficient of tin, $\log (a_2/N_2)$, is also reduced in the same region, but the effect is not so apparent because the $\log (a_2/N_2)$ values are normally rather small for all alloys rich in tin. This reduction of the activities of zinc and tin in alloys rich in

tin may possibly be due to the formation of a weak compound in the liquid alloy. The freezing-point diagram shows no solid compound, but it might be mentioned that the electromotive-force method is a much more delicate means for determining activities than the average alloy freezing-point diagram now in existence.

Comparison of the Activity Curves for Various Alloys

Of the five liquid metal systems investigated, three exhibit simple type $\log (a/N)$ curves for which the activities of each component are greater than demanded by Raoult's law. These are cadmium-tin, cadmium-

lead. and cadmium-zinc. The system zinc-tin shows too high activities, but the curve is not quite so simple as in the three cases just mentioned. The system cadmium-bismuth is still more complicated. Certain amalgams also show abnormally high activities for each component. Thus the vapor pressure of mercury at 320° from amalgams of zinc, bismuth, gold, tin and lead, is abnormally high.2i,2j,2k

If the internal pressure difference between the two components of an alloy is responsible for their abnormal increase in activity, there should be some parallelism between the values of these two quantities in various alloys.

The internal-pressures of liquid zinc, cadmium, tin, lead and bismuth can be estimated⁵ from existing surface-

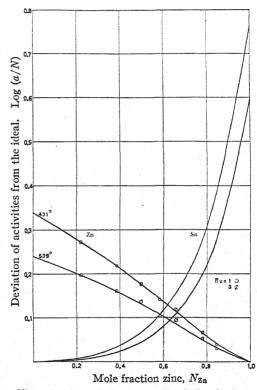


Fig. 10.—System, zinc-tin. Deviation from the laws of the perfect solution. The horizontal line $\log (a/N) = 0$ corresponds to Raoult's law

tension and density data⁴ on these metals. The values at 450° of the quantity $E_{\sigma}/V^{1/2}$ where E_{σ} represents the surface energy and V the molal volume, are as follows: zinc, 380; cadmium, 274; tin, 222; lead, 182; bismuth, 150. In Table XII values of $\Delta(E_{\sigma}/V^{1/2})$ for certain alloys are

⁵ Harkins, Proc. Nat. Acad. Sci., 5, 566 (1919).

compared with the corresponding activity coefficients of cadmium and tin from these alloys.

TABLE XII

	ACTIVIT	y Coefficie	nts in Vari	ous Alloys	i	
. **	t no		$\log(a/N)$ for C		Int. press. diff.	
Alloy	°C.	$N_{\rm Cd} = 0.0$	$N_{\mathrm{Cd}} = 0.1$	$N_{\mathrm{Cd}} = 0.2$	$\Delta(E_{\sigma}/V^{1/2})$	
Cd-Sn	483	0.28	0.228	0.185	52	
Cd-Pb	480	.55	.455	.369	92	
Cd-Zn	466	.80	.540	.373	106	
			Log(a/N) for	Sn		
		$N_{\rm Sn} = 0.0$	$N_{\rm Sn} = 0.1$	$N_{\rm Sn} = 0.2$		
Sn-Zn	466	0.72	0.459	0.274	158	
Sn-Cd	483	.33	.250	.184	52	

It will be observed that in the case of both the cadmium and the tin alloys there is a parallelism between the log (a/N) and the $\Delta(E_{\sigma}/V^{1/3})$ values. The two series are not strictly proportional, but there is enough evidence to show that a difference of internal pressure is a large factor in determining activities in liquid metal systems.

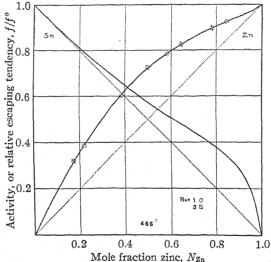


Fig. 11.—Activity curves for the system, zinc-tin at $466\,^{\circ}$

A similar comparison might be made of the escaping tendencies of zinc from zinc-cadmium and zinc-tin alloys, but the results would mean very little, since in the latter case the $\log{(a/N)}$ curve is quite irregular and is probably complicated by compound formation. The internal-pressure theory requires that solutions of zinc with lead, and zinc with bismuth show still greater positive deviations from ideal behavior than have been found in the case of cadmium-lead or zinc-cadmium solutions. The theory is

corroborated by the fact that both zinc-lead and zinc-bismuth alloys form two liquid phases. The critical mixing temperature, for these two systems are given in Landolt-Börnstein "Tabellen" as about 850° for zinc-bismuth and about 950° for zinc-lead. This temperature should be higher for zinc-bismuth if internal pressures were the only factor, but it is possible that the activities of both components are considerably reduced by compound formation just as has been found in cadmium-bismuth alloys. The fact that 2 phases are formed, however, is strong evidence in favor of the internal-pressure theory.

The Heat of Mixing

The heat of the reaction taking place in a galvanic cell may be readily calculated from measurements of the electromotive force of the cell at different temperatures. Calculations made using the electromotiveforce data obtained in the present research, give the heat absorbed during the transfer of 1 mole of pure liquid metal from the pure state to an alloy of known composition. If, for example, H_1 is the molal heat content of pure zinc, and \overline{H}_1 is the partial molal heat content of zinc in a given zinc alloy, then according to the so-called Kirchhoff equation $\overline{H}_1 - H_1 = 2.303$ - $RT^2 \frac{\mathrm{d} \log (a_1/N_1)}{\mathrm{d}T}$, where the values of log (a_1/N_1) are those given earlier in this article. This equation is applicable also to the second component of the alloy; thus $\overline{H}_2 - H_2 = 2.303~RT^2 \frac{\mathrm{d} \log{(a_2/N_2)}}{\mathrm{d} T}$. The Helmholtz equation may also be used to calculate the partial molal heat of dilution of that component with respect to which the cell is reversible. Thus, $\bar{H}_1 - H_1 =$ nF[T.(dE/dT)-E], where n is the valence of the reacting ion, and F is the Faraday constant, namely 23074 calories per volt-equivalent. The quantity $\overline{H}-H$ has been defined as the relative heat content, \overline{L} , of one component of an alloy of some definite composition.6 The absolute values of H and of \overline{H} have no interest in the present connection; it is only the heat effect accompanying the reaction which is important.

The partial molal heats of dilution of the more electropositive component of each alloy system have been obtained in the two ways—by applying the Helmholtz equation to the individual electromotive values, and then plotting these heats and interpolating at even mole fractions, and also by using the Kirchhoff relation with the $\log (a/N)$ values at these even mole fractions. The heat values obtained by these two methods have been averaged and the results are recorded below. In general the agreement between the two sets of values was just about proportional to the average deviation of the experimental $\log (a/N)$ values from the accepted smooth curves. If these points had exactly fitted the $\log (a/N)$ curves there would

⁶ Randall and Bisson, This Journal, 42, 347 (1920).

of course have been no discrepancy between the 2 sets of heat values. The Kirchhoff equation is the only one applicable to the less electropositive component of the alloy.

The accuracy of the heat values depends upon the size of the temperature interval. For example, in the neighborhood of 500°, an error of 0.0001 volt in one of the electromotive-force values produces an uncertainty of 25 calories in the heat effect when the temperature interval is 140°, about 50 cal. when the temperature interval is 70°, and about 100 cal. when this interval is only 35°. Calculations of the partial molal heats of dilution for each component of the systems cadmium-tin, cadmium-lead, cadmium-zinc and zinc-tin have been made for two or three temperature intervals in the attempt to determine (1) the relation between the heat of mixing and the deviation from the laws of the perfect solution, and (2) how the heat of dilution changes with the temperature.

The heat values are recorded in Table XIII. In the first line it will be seen that when 1 mole of pure liquid cadmium is added to a very large amount of pure liquid tin at the same temperature, the heat absorbed amounts to 1360 calories. Similarly, if 1 mole of pure liquid cadmium is added to a very large amount of a cadmium-tin alloy in which the mole fraction of cadmium $(N_{\rm Cd})$ is 0.3, only 830 calories will be absorbed. It will be noticed that certain values in the third column of Table XIII are in parentheses. These values are somewhat uncertain. All the values in this column are extrapolated from the data in the remaining columns.

Table XIII Summary of Partial Molal Heats of Dilution, $\overline{H}-H$ In Calories

					~~~~~								
		Temp.		$\mathbf{N}$	Iole fr	action	of th	e solu	te na	međ			
Solute	In alloy	°C.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Cd	Cd-Sn	431-585	1360	1170	1000	830	650	480	320	190	100	40	0
		431-544	1400	1210	1030	840	650	460	300	180	80	30	0
		483-544	1470	1280	1100	920	740	560	410	270	140	40	0
Sn	Cd-Sn	431-585	1800	1450	1090	790	530	340	190	90	30	10	0
*		431-544	1800	1480	1170	870	600	370	210	95	35	10	0
		483-544	(2500)	(1800)	1280	900	590	370	220	110	40	10	0
Cd	Cd-Pb	432 - 572	2150	1820	1510	1220	950	720	510	300	140	50	0
		480-544	2300	1960	1620	1280	1040	800	600	410	240	70	0
Pb	Cd-Pb	432 - 572	3500	2580	1770	1160	720	440	270	150	70	15	0
		480-544	3600	2660	1860	1250	820	550	350	220	120	45	0
Cd	Zn-Cd	435-540	(2000)	1580	1260	1000	780	580	420	280	140	60	0
		466-540	(1900)	1490	1180	940	740	560	400	260	140	60	0
Zn	Zn-Cđ	435-540	2500	1900	1380	980	650	460	320	220	140	70	0
		466-540	2500	1900	1400	1050	720	500	350	240	150	70	0
Zn	Zn-Sn	431-570	2490	2220	1940	1650	1370	1110	840	600	350	140	0
		466-539	2380	2120	1850	1580	1310	1060	800	560	340	140	0
		431-466	2560	2290	2020	1720	1420	1140	850	600	370	150	. 0
Sn	Zn-Sn	431-570	4500	3340	2170	1340	850	530	310	160	70	20	0
		466-539	4600	3060	1990	1300	840	510	300	150	70	20	0
		431-466	(4100)	3200	2340	1560	1000	620	370.	190	70	20	0

Inspection of this table shows that in general the various sets of heat values, calculated from different temperature intervals, are concordant.

As a rule the discrepancies are not larger than the error of measurement. It must, therefore, be concluded that the change in the heat of dilution with temperature is fairly small.

The heat values given in the fourth column of Table XIII, under the heading "0.0," correspond to the heat absorbed when 1 mole of pure liquid A is added to a very large amount of pure liquid B. These particular heats of dilution bear a simple relation to the differences between the internal pressures of the two components, A and B. In order to show this relationship the values of Col. 4 are averaged and recorded in Table XIV together with the corresponding internal-pressure differences.

TABLE XIV

Internal Pressure Difference and Heat of Mixing when 1 Mole of Liquid A is Added to a Very Large Amount of Liquid B

		Heat absorbed		al press. di		_
$\boldsymbol{A}$	$\mathcal{B}$	$\overline{H}-H$ Cal.	$\Delta(E\sigma/V^{1/3})$	$\Delta(\gamma/V^{1/3})$	$(\overline{H}-H)/\Delta(E\sigma/V^{1/3})$	$(\overline{H}-H)/\Delta(\gamma/V^{1/3})$
Cd	Sn	1400 = 60	52	58	$27.0 \pm 1.2$	$24.1 \pm 1.0$
Cd	Pb	2200 = 50	92	93	$24.0 \pm 0.6$	$23.6 \pm 0.6$
Cd	Zn	$1950 \pm 200$	106	94	$18.4 \pm 1.9$	$20.8 \pm 2.1$
Sn	Cd	1800 = 50	52	58	$34.6 \pm 1.0$	$31.0 \pm 0.9$
Sn	Zn	4550 = 150	158	152	$29.0 \pm 1.0$	$30.0 \pm 1.0$

In this table two criteria have been used for estimating internal pressure. The ratios given in the last two columns are approximately constant, being especially so in the last column. The discrepancies in these ratios are no greater than the uncertainty of the internal-pressure values themselves. It may be concluded, therefore, that in liquid alloys which are not complicated by compound formation between the components, the heat of mixing is directly proportional to the internal-pressure difference. A comparison similar to that in Table XIV might be made in the case where zinc is the solute, that is, in zinc-tin and zinc-cadmium alloys. The results, however, would mean very little, since the activity curves of zinc in zinc-tin alloys are not of the simple type, and very probably the internal-pressure difference is in this case not the only factor which operates to produce departures from Raoult's law.

It has been shown that where an alloy solution is free from compounds between the components, both the deviations from Raoult's law and the partial molal heats of mixing are proportional to differences of internal pressure. It follows, therefore, that these first two quantities are closely related. For a given solute in different liquid alloy systems the partial molal heat of dilution is very nearly directly proportional to the deviation of this solute from Raoult's law.

This research was undertaken at the suggestion of Professor Joel H. Hildebrand. I wish in conclusion to express my sincere appreciation of his personal kindness and stimulating counsel throughout the investigation.

#### Summary

Accurate determinations of the activities of liquid zinc, cadmium, tin, lead and bismuth in five binary-alloy systems have been made at temperatures ranging from 400° to 600°.

With the single exception of the system, cadmium-bismuth, which gave a very complicated type of activity curve, all the alloy systems investigated showed escaping tendencies or activities greater than required by Raoult's law. In regard to departures from this ideal solution law, and also in regard to the heats of mixing, the results of this research furnish strong evidence for the validity of the internal-pressure theory as applied to liquid metal systems.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

#### THE EFFECT OF PRESSURE ON OVERVOLTAGE

By S. J. Bircher and William D. Harkins Received September 6, 1923

In 1919 MacInnes and Adler¹ published a theory of overvoltage based in part upon the theory of Möller² and in part upon the then unpublished work of Goodwin and Wilson. Since then the latter have published their data,³ which indicate that overvoltage increases as the pressure is reduced, and with extreme rapidity at low pressure.

In 1914, Harkins and Adams⁴ determined the effect of pressure on the hydrogen overvoltage of mercury. They state, "Keeping the current constant, the pressure in the hydrogen cell may be raised from one atmosphere to three and reduced to twenty millimeters, without producing any significant change in the potential between the cathode and the hydrogen electrode. In such a system the potential values are never absolutely constant. They may undergo a progressive gradual change or be subject to slight eccentric variations, but such changes can in no way be correlated with changes in pressure." Newbery found that oxygen overvoltage is practically constant in the range between 1 and 100 atmospheres.⁵

It will be noted that the conclusions reached by Goodwin and Wilson, and by Harkins and Adams are quite contradictory, but it is thought that the data and discussion herein contained, which are much more closely in agreement with the latter, indicate how both conclusions have been reached.

- ¹ MacInnes and Adler, This Journal, 41, 194 (1919).
- ² Möller, Z. physik. Chem., 65, 226 (1909).
- ³ Goodwin and Wilson, Trans. Am. Electrochem. Soc., 11, 172 (1921).
- ⁴ Harkins and Adams, Thesis, Library of the University of Chicago, 1914.
- ⁵ Newbery, J. Chem. Soc., 105, 2419 (1914).

Both papers referred to above stress the necessity for expressing the overvoltage as a difference between the potential of the cathode and that of a reversible hydrogen electrode under the same conditions. Though this is the usual definition of overvoltage, the method of measuring such differences directly presents certain difficulties due to the non-reversibility of the hydrogen electrode at low pressures. An analysis of the experimental conditions employed by both Goodwin and Wilson, and Harkins and Adams suggested the possibility of studying certain factors individually without violation of any of the conditions inherent in the usual procedure. This analysis was undertaken after preliminary work upon the effect of pressure on the nickel cathode which appeared at first to agree with the conclusions of Goodwin and Wilson. This work was later found to be incorrect.

The effect of pressure on overvoltage as usually defined involves two distinct effects, that on the hydrogen electrode and that on the cathode potential. The practice of separating these effects when the influence of conditions other than pressure upon overvoltage is studied is quite general. It was therefore our purpose to study these effects separately and then to combine the numerical results.

In determining the effect of pressure on the hydrogen electrode potential, the hydrogen electrode and the mercurous sulfate electrode, used as a reference electrode, were in communication in the same pressure bottle. Sulfuric acid of  $0.1\,N$  concentration was used throughout and the hydrogen was prepared by the method of Cooke and Richards. Connection between the two electrodes was made by a column of sulfuric acid sufficiently long to insure the absence of mercury ions in the hydrogen electrode vessel during the time required to make the measurements.

From the data of Table I it is to be noted that the potential of the hydrogen electrode decreases as the pressure is reduced, and down to at least 100 mm, the decrease is quite close to that demanded by the Nernst formula. The accuracy of these values is well within the limits that Goodwin and Wilson, or Harkins and Adams, attained in measuring overvoltage. The greater difficulty experienced in maintaining steady potential values for the hydrogen electrode when the pressure is quite low is due to several The rate at which the hydrogen is introduced and the size of the bubbles admitted tend to produce fluctuations in pressure. Any differences in the pressure of the hydrogen before and after it enters the cell would have a similar effect, because of volume changes. The greater tendency toward ebullition at the lower pressures may cause irregularities in the pressure due to irregular bubble emission. If the capacity of the hydrogen electrode is small or if it is not sufficiently well saturated with hydrogen it may cease to function as a hydrogen electrode entirely at low pressure. The potential under such conditions becomes quite positive-



⁶ Cooke and Richards, Am. Chem. J., 10, 81 (1888).

about that of the single potential of platinum in sulfuric acid. In so far as the pressure conditions are favorable to equilibrium conditions the potential of the hydrogen electrode is a function of the partial pressure of the hydrogen.

In order to define certain terms and conditions, several factors will be discussed before dealing with the effect of pressure on the potential of the cathode.

The term reduction in pressure may be interpreted in either of two ways. It may refer to changes in the total pressure of the gases above the electrolyte irrespective of their nature or number, or to the change in the partial pressure of some one gas without a change in the total pressure of the gases in the system. The potential of the hydrogen electrode is assumed to be dependent only upon the partial pressure of the hydrogen, whether that is produced by a change in the total pressure of pure hydrogen or by varying the percentage of hydrogen in the mixture of gases present in the system. The methods used for the study of the effect of pressure on the potential of the cathode are such that both the partial pressure of the hydrogen and the total pressure in the system vary. This makes it necessary to determine the part that each of these two factors contributes to the potential changes noted. If, as in the case of the hydrogen electrode, the potential of the cathode is dependent upon the partial pressure of the hydrogen and is independent of the total pressure, and the overvoltage increases rapidly at low pressure as observed by Goodwin and Wilson, it should then be possible to increase the polarization of a cathode which exhibits a certain potential when operating in an atmosphere of pure hydrogen by replacing this gas with another gas such as nitrogen. Experience has not supported this conclusion. According to the Nernst equation the potential of the hydrogen electrode becomes more positive as the pressure is reduced, and the data of Goodwin and Wilson indicate that decreased pressure makes the cathode more negative. According to this it may be assumed that pressure need not change the cathode potential in the same direction as it affects the potential of a reversible hydrogen electrode.

The use of the hydrogen electrode as an anode in work at low pressures involves certain factors not involved in other work on overvoltage. At atmospheric pressure there is a limit to the amount of current which may be passed through a cell having a hydrogen electrode as an anode without polarizing the anode. It has already been mentioned that the hydrogen electrode itself may become less stable at low pressures. It is therefore concluded that if a hydrogen electrode is used as the anode at low pressure the possibility of polarization is much greater. This makes it advisable to use an electrode with large hydrogen capacity so that the oxygen liberated per unit area will be small. The area of the platinum base is not the only factor which determines the capacity of the electrode for the sorption of

hydrogen. The nature of the platinum black deposit is also important. The capacity of electrodes may be compared by noting the time it takes for bubbles to appear if the electrolyzing circuit in which they are serving as electrodes is reversed.

The use of hydrogen anodes of large capacities makes the time required for the establishment of the equilibrium potential after a change in pressure much longer. With the added danger of oxygen polarization when the electrode serves as an anode it is impractical to use the anode to determine the reversible hydrogen electrode potentials at low pressure. Although such hydrogen anodes are more sluggish in attaining the reversible hydrogen electrode potential, their potentials are much steadier and consequently the current is much more constant than could be obtained with anodes of other types.

The design of the cathode is important in the investigation of overvoltage, and certain requirements are worthy of discussion. The danger of polarizing the anode has led some investigators to use a small cathode. There are two errors which attend this use of very small electrodes. The first has its origin in the close relation of overvoltage to surface tension. some investigations the electrodes have been discs of metal surrounded by glass, shellac, or other supporting and insulating materials. Now it is known that with a mercury electrode the bubbles tend to form between the glass and the mercury, so it is logical to assume that with other metals also the potential may be affected by the presence of a second phase with a different surface energy. There is a second error involved and this may be greatest when a study of the effect of pressure is made. The use of a cathode so small that a bubble is large compared with the size of the cathode may introduce a condition quite foreign to that met with in ordinary large electrodes. The lead cathode used by Goodwin and Wilson⁷ had an area of 0.0033 sq. cm., which is small compared to the size of bubbles which may be liberated. This is especially true at low pressures where the volume of the gas is great.8 It is better to use a very large anode than to introduce uncertainty of conditions by the use of small cathodes.

In the present work the effect of pressure on the potential of the cathode has been studied at two current densities at least for each of the metals used by Goodwin and Wilson. The cathodes used included mercury, the metal investigated by Harkins and Adams. For reasons given in a previous paper the current densities were selected without reference to the number of bubbles being liberated per second. For each metal in Tables

⁷ Ref. 3, p. 173.

⁸ It is important to note the fact that overvoltage is peculiarly sensitive to variations in the experimental conditions, so certain properties or relations are often cited as characteristic of overvoltage even though they have been found only by the use of highly specialized conditions.

II, III and IV a description of the cathode is given together with data on current density, the cathode potential and the overvoltage. The overvoltage values were obtained by subtracting the potential of the reversible hydrogen electrode at the given pressure from the cathode potential at the same pressure.

The cathode potentials are practically constant at all pressures studied except for temporary fluctuations. These fluctuations will be discussed

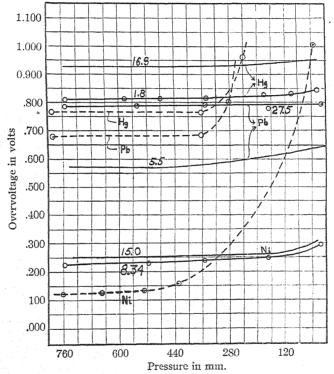


Fig. 1.—Relation of the hydrogen overvoltage to pressures of one atmosphere or less. The dotted lines represent the data of Goodwin and Wilson, the full lines, the data of the present paper. Two full lines are given for each metal; the higher line represents the higher current density. The two lines for nickel are close together, which indicates that at 20° an increase of current density is much less effective in increasing the overvoltage of nickel than in the case of the other two metals. The current densities for the respective lines are given in the figure except that the numbers for mercury give the currents instead of current densities

in considering the conclusions reached by Harkins and Adams. The overvoltage shows a slight increase paralleled by a decrease in the potential of the reference electrode. The order of magnitude of these changes in overvoltage is about 50 millivolts for a change from atmospheric pressure to a partial pressure of 11 mm. According to Goodwin and Wilson, correspond-

ing changes produce at least 850 millivolts' difference in overvoltage. For comparison, the values of Goodwin and Wilson are plotted in Fig. 1 by lines represented by dashes while the data of the present paper are represented by continuous lines.

The conclusion reached by Harkins and Adams that pressure has no effect on overvoltage, except for eccentric variations which they could not correlate with pressure, is probably due to the relatively small variations that do occur compared to the unsteadiness otherwise associated with overvoltage potentials. We have been able to correlate many such fluctuations with the changes of *total* pressure. In discussing the use of the hydrogen electrode as the anode we have indicated reasons for the non-reversibility of the hydrogen anode when used under the conditions peculiar to work on the pressure effect.

Table I

Effect of Pressure on the Potential of the Hydrogen Electrode

FECT OF	PRESSURE	ON THE	POTENTIAL	OF THE I	ADROGEN ELECTRODE
Cell:	$H_2 \mid 0.1 \ N$	H ₂ SO ₄   F	Ig ₂ SO ₄   Hg		Temperature, 0°
Time H. M.			tial pressure f hydrogen	Potenti obs.	al Potential cale.
11:50	7.	57	753	0.7552	2
12:37				.755	1
2:00				.755	5
2:33				.7550	0.7554
5:25	3'	75	371	.748	7
6:00				.7480	) **
6:25				.7479	)
7:10				.7479	0.7468
9:00	1	04	100	.732	2
9:15				.732	1
9:25				.732	<b>4</b>
10:05				.732	4 0.7313
10:58		9	4.5	.679	5
11:15				.677	0
11:30				.675	9
11:37				.675	5
12:00				.675	5 0.6952

The data of the present paper show fluctuations at any one pressure which might be termed eccentric. It was often observed that as the pressure was being reduced, the cathode potential would increase and then later decrease. However, more careful observation shows that such increases are due to the rapid expansion and later escape of a bubble already on the cathode. (See Table II.) Such changes are more noticeable when only one bubble is present on the cathode, particularly in the case of mercury. Here the small bubbles which form around the edge later gather to form a large bubble at the top of the meniscus. The variation of the potential during the growth and escape of one of these bubbles is several millivolts.

The cathode potential becomes more negative as the bubble grows until it is large enough to roll upon the surface as the small bubbles unite with it.

TABLE II

Effect of Pressure on the Potential and the Overvoltage of a Mercury Cathode

(The data for cathodes of lead and nickel are given in Fig. 1)

Area of cross section of containing tube: 0.1452 sq. cm. Measurements at the stated currents in microamperes.

16.			1.77	5	
Pressure Mm.	Cathode potential	Over- voltage	Pressure Mm.	Cathode potential	Over- voltage
750.5	1.6810		750.3	1.5652	
	1.6817	0.9263		1.5652	0.811
599.5	1.6817		581.3	1.5652	
	1.6790	.9263		1.5652	
				1.5652	.812
473.0	1.6791				
	1.6798	.9295	459.0	1.5652	
				1.5650	
366	1.6796			1.5652	.815
	1.6800	.9338			
			348	1.5653	
245	1.6798			1.5653	.819
	1.6782	.939			
			183.5	1.5645	
109	1.6757			1.5657	. 830
	1.6767				
	$1.6740^{a}$	•	103	1.5640	
	1.6751	. 947		$1.5590^a$	
				1.5589	. 834
20	1.6633				
	1.6500		19	1.5430	
	1.6595	. 954		1.5400	
				1.5420	
				1.5440	
				1.5480	
				1.5480	.843

^a A large bubble was observed to leave just *before* the reading was taken. Note the *lowering of the potential* which this caused.

When this occurs the potential decreases slightly at first and then very rapidly as the bubble escapes. The galvanometer deflections indicate the tendency for the bubble to escape several seconds before the bubble leaves the cathode. These observations as to the effect of bubble size on overvoltage do not seem at first to be in agreement with the effects of bubble size on overvoltage as observed by MacInnes and Adler. However, the conditions of the two experiments are quite different so that differences are to be expected. It is planned to extend the work connected with bubbles on mercury and discuss the subject in a later paper.

Two conditions may produce apparent increases in overvoltage of con-

siderable magnitude. There is a possibility that the reference hydrogen electrode may cease to function reversibly and may thus revert to a platinum electrode. A second possibility is that a large fraction of the cathode may become covered with hydrogen bubbles at the lower pressures. This may cause an apparent increase in overvoltage in two ways. First, this layer of hydrogen gas would introduce a resistance in the electrolyzing circuit. Second, if the bubble merely insulates part of the cathode area the overvoltage would increase because of the increased current density. Such variations would be quite apparent if the cathode area were small compared with that of one bubble.

#### Summary

- 1. The effect of pressure on the *potential* of a cathode at which hydrogen is being liberated is in general very small at pressures between 760 mm. and 11 mm. The slight changes which occur are due to bubble expansion and consequent shielding of the cathode, and to increased stirring caused by the more rapid bubble liberation at low pressure.
- 2. Overvoltage defined with reference to a reversible hydrogen electrode increases as the pressure is decreased. This increase is paralleled entirely by a decrease in potential of the hydrogen electrode. Between 760 mm. and 11 mm. the range of variation of the overvoltage is about 50 millivolts.
- 3. The data of the present paper are of interest in connection with the theory of overvoltage presented by MacInnes and Adler.1 According to them the overvoltage (E) is given by the equation,  $E = (3RT/2pr) \cdot \gamma$  in which p is the pressure in the bubbles, r their radius, and  $\gamma$  the surface tension of the liquid. They reach the conclusion that the bubble radius is practically constant with variation of pressure, so the overvoltage should vary inversely as the pressure and thus increase very rapidly as low pressures are approached. The present work indicates that the overvoltage increases with decrease of pressure only to the extent that the hydrogen electrode potential decreases, that is, as the logarithm of the pressure. On the other hand, in earlier work in this Laboratory the overvoltage of a number of inactive metals was found to have the same temperature coefficient, and to decrease 2 mv. per degree in 0.1 N sulfuric acid. seems to point to the surface tension of the liquid as an important factor in overvoltage. The above facts, taken together, seem to indicate that the theory of MacInnes and Adler is a partial rather than a complete theory of overvoltage.
- 4. Care was taken to avoid stirring of the liquid around the cathode, so the smallness of the increase of overvoltage with decrease of pressure cannot be due to the effect of stirring. The considerable lowering of overvoltage of the ordinary type produced by stirring was pointed out by Harkins and Adams⁴ in 1914.

5. The overvoltage at a mercury meniscus in dil. sulfuric acid was found to *increase* as the large bubble at the top of the meniscus becomes larger, and to *decrease* suddenly when the bubble escapes.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

#### THE INDIVIDUAL THERMODYNAMIC PROPERTIES OF IONS

By J. N. Brönsted

RECEIVED SEPTEMBER 8, 1923

## The Principle of the Specific Interaction of Ions

The available information regarding the thermodynamic properties of salt solutions, as manifested through electrometric and freezing-point measurements and particularly through the measurement of the solubilities of sparingly soluble salts in salt solutions, leaves no doubt that these properties even at high dilution are largely dependent upon the nature of the solution considered. It is not a question here of the typical deviations depending upon the valence type of the various solutes, but of deviations shown by isotypic ions in dependency of their individual nature. In spite of the fact that these peculiarities have, at first sight, a rather random character, a closer examination has shown that an important simplicity prevails, which has been formulated by the writer as the principle of the specific interaction of ions.

The basis and the applicability of this principle have been elaborately presented in a previous article, where emphasis was laid upon the possibility of splitting the activity coefficient into two factors, a coefficient of interaction and a salting-out coefficient, the latter of which should be a function of the solvent only. This devision is valuable in cases where the possibility exists of determining separately the ratio of the two factors such as was shown in the previous article when salts of different valence type are used for saturating salts in solubility measurements. The calculation of these ratios requires a high degree of accuracy in the experimental determinations and but very slight deviations from the underlying principles because the equations for the calculations have such a form as to be highly sensitive towards such deviations.

The contents of the principles in question may, however, be expressed more simply without the above-mentioned division of the activity coefficient into its two factors. Let  $A_1B$  and  $A_2B$  represent two solvent salts with an anion (B) in common, and having the same equivalent concentration. Let X be an arbitrary cation and Y an arbitrary anion, present

¹ Brönsted, This Journal, 44, 877 (1922).

in small amount in the two solvents. Then our principle can be stated by the following expressions.

$$\frac{f_{\mathbf{X}(\mathbf{A}_1\mathbf{B})}}{f_{\mathbf{X}(\mathbf{A}_2\mathbf{B})}} = F(\mathbf{A}_1, \mathbf{A}_2) \tag{1}$$

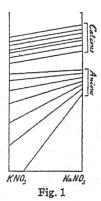
and

$$\frac{f_{Y(A_1B)}}{f_{Y(A_2B)}} = F(A_1, A_2, Y)$$
 (2)

where F represents some indeterminate function. That is to say, the ratio of the activity coefficients of the same cation in two equally strong solutions having an anion in common is a function only of the nature of the two cations of the solvents. And the ratio of the activity coefficients of the same anion in two equally strong solutions having an anion in common is a function of the nature of the anion considered and the cations of the two solvents. In neither case does the nature of the common anion of the solvents enter.

It need hardly be added that the validity of the equations will remain unaffected if throughout the above statement the terms cations and anions be interchanged.

The meaning of this law appears clear by considering the accompanying diagram (Fig. 1). The ordinates indicate  $\ln f$ , that is, the logarithms of the activity coefficient of various cations and anions of the same type. From the two vertical lines indicated by NaNO₃ (A₁B) and KNO₃ (A₂B) the values of  $\ln f$  in the corresponding solution are read, reckoned from arbitrary standard values. The  $\ln f$  values for any particular ion in the two solvents are given by the intersections of the corresponding straight lines with the two axes. In accordance



with Equation 1 the lines belonging to cations are all parallel, while in the case of anions, according to Equation 2 the slopes may be different. The shape of the curve remains unchanged when the anion of the solvent changes as, for example, in changing from potassium and sodium nitrate to potassium and sodium chloride solutions.

In the verification of the principle of specific interaction given in the previous paper the ion X in Equation 1 was changed not only in nature, its type being kept constant, but also in its general valence type. In fact, the assumption of the validity of Equation 1 under these conditions was the basis of the calculation of the ratios of interaction and salting-out effects. No experiments, however, have hitherto been available to show the applicability of Equation 1 to cases of different valence of the ions  $A_1$  and  $A_2$ . In the last part of the present paper evidence will be furnished which will show that Equation 1 is valid also for different valence of  $A_1$  and  $A_2$ , at least when X has a constant valence, and probably also when the valence of X changes.

Equations 1 and 2 and Fig. 1 furnish in reality a concise and adequate statement of what on the basis of the principle of specific interaction can be said regarding the influence of the natures of ions upon their thermodynamic properties.

It may be added that the change in the activity coefficients of a salt passing from  $A_1B$  to  $A_2B$  is given simultaneously when we remember that

$$\nu \ln f = \Sigma \nu' \ln f' \tag{3}$$

where f is the activity coefficient of the salt, f'f''. . .the activity coefficient of the ions of the salt,  $\nu'\nu''$ . . .the corresponding numbers of ions in one molecule and  $\nu = \Sigma \nu'$ .

## The Linear Variation of the Activity Coefficients

The principle of the specific interaction of ions was based on the idea that ions of the same valence must be influenced uniformly by ions of their ' own sign. The individualities in salt solutions, therefore, ought to be attributed to the interaction of ions of opposite sign, varying with the nature of these ions, and to a more general effect upon all ions present, namely the salting-out effect or solvent effect, depending merely on the salt solutions serving as solvents. A continued study of the fundamental considerations of this principle has shown, however, that several of the results obtained for its corroboration can also be obtained by use of another simple principle, which we shall introduce in the theory of the dilute salt solutions as the principle of the linear variation of the activity peculiarities. This principle may be stated as follows. In a dilute salt solution the osmotic deviations of the solutions and the activity deviations of any ion from an ideal value is, at constant composition of the dissolved salt mixture, a linear function of its total concentration and, at constant total concentration of an isotypic mixture, a linear function of its composition.

In this statement the expression "activity deviations" from an ideal value is understood to mean  $ln(f/f_i)$ , where f is the activity coefficient of the ion considered and  $f_i$  the ideal activity coefficient depending only upon the type of salt and the total concentration.

The first part of the above assumption, namely that at constant composition the osmotic and activity deviations are linear functions of the concentration, has already been advanced previously² for the case of pure salt solutions of univalent salts. The equation

$$1 - \varphi = \alpha \sqrt{c} + \beta c \tag{4}$$

was suggested to hold for solutions up to about  $0.1\,N$  concentration. In this equation  $\alpha$  is a universal constant the value of which at  $0^{\circ}$  is about 0.32 and varies but little with the temperature, while  $\beta$  accounts for the individualities. The ideal value of the activity coefficient is

$$\ln f = -3\alpha\sqrt{c} \tag{5}$$

² Brönsted, This Journal, 44, 938 (1922).

This part of the principle is, therefore, only an extension of the applicability of Equation 4 to valence types other than the uni-univalent, in which case it has already been verified. It remains to be shown that several of the results obtained previously on the basis of the principle of the specific interaction can be derived from the second part of the new principle.

For this purpose we shall introduce the thermodynamic equation³  $x \, d \ln f_{\text{Na}} + (1-x) d \ln f_{\text{K}} + d \ln f_{\text{Cl}} = 2d\varphi$  (6)

as applied to a mixture of sodium and potassium chloride solutions of constant total concentration. By introducing our assumption of a linear variation of the deviation coefficients with x

$$\frac{\mathrm{d} \ln f_{\mathrm{Na}}}{\mathrm{d} x} = a, \quad \frac{\mathrm{d} \ln f_{\mathrm{K}}}{\mathrm{d} x} = b, \quad \frac{\mathrm{d} \ln f_{\mathrm{Cl}}}{\mathrm{d} x} = c, \quad \frac{\mathrm{d} \varphi}{\mathrm{d} x} = d,$$

where a, b, c and d are constants, we obtain from Equation 6 when x = 0, the expression, b = 2d - c; and when x = 1, a = 2d - c and therefore for all values of x

$$\frac{\mathrm{d}\ln f_{\mathrm{Na}}}{\mathrm{d}x} = \frac{\mathrm{d}\ln f_{\mathrm{K}}}{\mathrm{d}x}.\tag{7}$$

in full conformity with Equation 1 and Fig. 1. By the same method as used in the previous paper³ we then derive

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \ln \frac{f_{\text{NaCl}(\text{NaCl})}}{f_{\text{NaCl}(\text{KCl})}}$$

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \ln \frac{f_{\text{KCl}(\text{NaCl})}}{f_{\text{KCl}(\text{KCl})}}$$
(8)

and therefore:

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \ln \frac{f_{\text{HCl(NaCl)}}}{f_{\text{Hcl(Kcl)}}}$$
(9)

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{S_{\text{AgCl(KCl)}}}{S_{\text{AgCl(NaCl)}}}$$
 (10)

These equations, by means of which freezing points of the solvents with an ion in common are correlated to activity coefficient and solubilities of salts possessing the same common ion, are identical with the equations derived on the basis of the principle of the specific interaction of ions. Also, the solubility equation of salts in hetero-ionic solvents, namely,

$$\frac{S_{\text{AgCl(KNO3)}}}{S_{\text{AgCl(NaNO3)}}} = \frac{S_{\text{TlCl(KNO3)}}}{S_{\text{TlCl(NaNO3)}}} \tag{11}$$

is easily arrived at by using Equations 8 and 9. So far, the principle of linear variation and the principle of the specific interaction are quite equivalent. The equation⁴

$$\frac{S_{\text{AgCl}(\text{KNO3})}}{S_{\text{AgCl}(\text{NaNO3})}} = \frac{S_{\text{AgCl}(\text{KClO3})}}{S_{\text{AgCl}(\text{NaClO3})}} \tag{12}$$

and the more general.

$$\frac{f_{\text{HCl(NaNO3)}}}{f_{\text{HCl(KNO3)}}} = \frac{f_{\text{HCl(NaClO3)}}}{f_{\text{HCl(KClO3)}}} \tag{13}$$

³ Ref. 1, p. 895. The notation used in that article will be followed here.

⁴ Ref. 1, p. 883.

are, however, not derivable from the principle of the linear variation of the activity peculiarities. For their derivation is required the validity of the principle of the specific interaction, as given by

$$\frac{f_{\text{Cl}(\text{NaCl})}}{f_{\text{Cl}(\text{KCl})}} = \frac{f_{\text{Cl}(\text{NaNO}_3)}}{f_{\text{Cl}(\text{KNO}_3)}} = \frac{f_{\text{Cl}(\text{NaClO}_3)}}{f_{\text{Cl}(\text{KClO}_3)}} = \dots$$

$$\frac{f_{\text{K}(\text{KCl})}}{f_{\text{K}(\text{KNO}_3)}} = \frac{f_{\text{K}(\text{NaCl})}}{f_{\text{K}(\text{NaNO}_3)}} = \frac{f_{\text{K}(\text{HCl})}}{f_{\text{K}(\text{HNO}_3)}} = \dots$$
(14)

Since in the previous paper Equations 5-10 have already been verified, we must assume that the fundamental considerations underlying them, as given by the two principles and Equation 1, are correct.

Equation 8 combined with Equation 15,

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = \frac{1}{2} \ln \frac{f_{\text{NaCl}(\text{NaCl})}}{f_{\text{KCl}(\text{KCl})}}$$
(15)

which is identical with Equation 24 in the previous paper, yields an important correlation between the activity coefficients of two salts with a common ion, namely

$$f_{\text{NaCl}(\text{NaCl})} f_{\text{KCl}(\text{KCl})} = f^{2}_{\text{NaCl}(\text{KCl})} = f^{2}_{\text{KCl}(\text{NaCl})}$$
(16)

and

$$f_{\text{NaCl}(\text{KCl})} = f_{\text{KCl}(\text{NaCl})} \tag{17}$$

The activity coefficient of sodium chloride, present in a small amount in a solution of potassium chloride is then seen to be identical with the

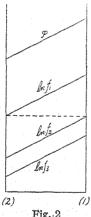


Fig. 2

activity coefficient of potassium chloride present in a small amount in a solution of sodium chloride of the same strength, this value being the geometrical mean of the activity coefficients of the two salts in their own solutions. The meaning of this is clearly illustrated by the accompanying diagram, Fig. 2, where the abscissa indicates the composition x of the mixture, and the ordinate  $\varphi$  and  $\ln f$ , and where, for instance, Salt 1 = NaCl, Salt 2 = KCl and Salt 3 = HCl. The four lines  $\varphi$ , ln f,  $ln f_2$  and  $ln f_3$  are drawn parallel, and  $ln f_{1(2)} = ln$ f2(1).

This result is reached by means of the principle of the linear variation only. This principle also leads to corresponding equations for mixtures of salts with no ion in common.

For this purpose we first use Equation 15

$$\varphi_{\rm NaCl} - \varphi_{\rm KCl} = \tfrac{1}{2} \ln \frac{f_{\rm NaCl\,(NaCl)}}{f_{\rm KCl\,(KCl)}}, \quad \varphi_{\rm KCl} - \varphi_{\rm KNO3} = \tfrac{1}{2} \ln \frac{f_{\rm KCl\,(KCl)}}{f_{\rm KNO3\,(KNO3)}}$$
 and thus

$$\varphi_{\text{NaCl}} - \varphi_{\text{KNOs}} = \frac{1}{2} \ln \frac{f_{\text{NaCl(NaCl)}}}{f_{\text{KNOs(KNOs)}}}$$
(18)

Moreover, from Equation 8,

$$\varphi_{\text{NaCl}} - \varphi_{\text{KCl}} = ln \frac{f_{\text{KCl}(\text{NaCl})}}{f_{\text{XCl}(\text{KCl})}}, \quad \varphi_{\text{KCl}} - \varphi_{\text{KNOz}} = ln \frac{f_{\text{KY}(\text{KCl})}}{f_{\text{KY}(\text{KNOz})}}$$

where X is an arbitrary cation and Y an arbitrary anion, we obtain

$$\varphi_{\text{NaCl}} - \varphi_{\text{KNO}_3} = \ln \frac{f_{\text{XCl(NaCl)}} f_{\text{KY(KCl)}}}{f_{\text{XCl(KCl)}} f_{\text{KY(KNO}_3)}}$$
(19)

Putting X = K and Y = Cl, this equation is reduced to

$$\varphi_{\text{NaCl}} - \varphi_{\text{KNO}_3} = ln \frac{f_{\text{KCl(NaCl)}}}{f_{\text{KCl(KNO}_3)}}$$
(20)

and for the reason of symmetry we also are allowed to write:

$$\varphi_{\text{NaCl}} - \varphi_{\text{KNO}_3} = ln \frac{f_{\text{NaNO}_3(\text{NaCl})}}{f_{\text{NaNO}_3(\text{KNO}_3)}}$$
(21)

By combining (18), (20) and (21) we obtain

$$\frac{f_{\text{NaCl(NaCl)}}}{f_{\text{KNO3}(\text{KNO3})}} = \frac{f^{2}_{\text{KCl(NaCl)}}}{f^{2}_{\text{KCl(KNO3)}}} = \frac{f^{2}_{\text{NaNO3}(\text{NaCl)}}}{f^{2}_{\text{NaNO3}(\text{KNO3})}}$$
(22)

or

$$\frac{f_{\rm Na(NaCl)}\,f_{\rm Cl(NaCl)}}{f_{\rm K(KNO_3)}\,f_{\rm NO_5(KNO_3)}} = \frac{f_{\rm K(NaCl)}\,f_{\rm Cl(NaCl)}\,f_{\rm Na(NaCl)}\,f_{\rm NO_3(NaCl)}}{f_{\rm K(KNO_3)}\,f_{\rm Cl(KNO_3)}\,f_{\rm Na(KNO_3)}\,f_{\rm No_5(KNO_3)}}$$

or

$$f_{\text{KNOs}(\text{NaCl})} = f_{\text{NaCl}(\text{KNOs})} \tag{23}$$

corresponding to Equation 17 for salts with a common ion.

#### Some Recent Work on Activity Coefficients

The question of the activity coefficients of salts has been discussed in a recent paper by Harned and Brumbaugh.⁵ To represent the concentration effect they use the equation

$$ln f = Ac - Bc^m (24)$$

of a form similar to that proposed by the writer, 2 namely,

$$lnf = a\sqrt{c} + bc \tag{25}$$

The two equations are, however, entirely different in that in (25) a is a universal constant, the peculiarities of the various salts being accounted for solely by the coefficient b, while in (24) A, B, and m are allowed to vary from one salt to another. As pointed out previously, an equation such as (24) does not fulfil the requirement, necessary from a theoretical point of view, of a uniform convergence of the values of  $\ln f$  for all salts, when the concentration approaches zero.

Equation 24, therefore, is to be looked upon as an empirically established expression by means of which, on account of the relatively great number of constants that may be varied independently, a rather close approximation to experimental results may be reached. The actual numerical values inserted for the constants in the equation exclude, however, its application at great dilution. Even if such an expression may be found to be helpful in some cases, it seems of more immediate importance to establish a theoretically corroborated formula for dilute solutions where

⁵ Harned and Brumbaugh, This Journal, 44, 2729 (1922).

the factors influencing the activity are still moderate in number. Equation 25 has no pretention of applicability at such high concentration, its limit being at about  $0.1\ N$  concentration for uni-univalent salts, and is not objectionable, therefore, that the minima for activity coefficients at high concentration cannot be computed with its help.

In the important question of the change of the activity coefficients in salt solutions of constant total concentration the ideas advanced by Harned are obviously in no agreement with the theory developed in this and previous articles on this subject by the writer.

It should be of some general interest to subject these ideas to a detailed discussion in order to make clear the thermodynamic or experimental requirements to be observed in developments of this kind.

In a series of solutions of the same concentration containing salts with a common ion, the activity coefficient of that ion is assumed by Harned to be constant. Accordingly, in 0.1 N solutions of sodium, potassium. hydrogen chloride, . . . and in mixtures of such chlorides the chlorine ion should possess the same activity coefficient. As replacement of potassium ion by hydrogen ion or another cation is assumed to exert no influence on the chloride ion, it is obvious on this basis that a partial replacement of the chloride ion by a nitrate ion would also have no influence, because we must assume that the greatest effect exists between ions of different sign. According to this point of view acceptance of the principle of Harned, namely, "the principle of the independent activity coefficients," would result in the assumption that all activity coefficients, at constant total concentration, depend only upon their own nature and not upon the nature of the solution containing them. This, indeed, was the conclusion drawn by Lewis and Randall.⁷ For thermodynamic reasons this conclusion, however, can be true only at ideal dilution, and in this region is included in the much simpler law that all activity coefficients are equal.

We now learn from the latest article by Harned and Brumbaugh that the Harned principle is to be interpreted somewhat differently. In equally strong solutions of sodium, potassium, hydrogen chlorides . . . and in their mixtures the chlorine ion is assumed to possess the same activity, but in their mixtures the activity coefficients of the constituent cations are assumed to vary. Furthermore, the activity coefficients of other cations introduced in small amounts are also assumed to vary from one solution to another. This assumption of Harned, although thermodynamically possible, is in peculiar contrast to the principle of the specific interaction of ions. For the theoretical reasons already stated, it is highly improbable, and furthermore it does not agree with experimental facts.

⁶ Ref. 5. The minima found by Harned and Brumbaugh and by M. Chow [This Journal, 42, 488 (1920)] in mixtures of potassium chloride and hydrochloric acid at low acid concentrations can hardly be looked upon as sufficiently established.

⁷ Lewis and Randall, ibid., 43, 1137 (1921).

Let us take, for example, solutions of sodium and potassium chlorides of equal concentration. Thallous chloride shows different solubility in these two solutions. This is possible with constant chlorine-ion activity if the thallous ion is affected differently by the sodium and the potassium ions. But if this influence is the only reason for the difference in solubility, such as the Harned theory assumes, then the same solubility ratio should be shown by all sparingly soluble thallous salt when using the corresponding sodium and potassium salt solutions as solvents. That is to say, we should expect

$$\frac{S_{\text{TICI}(\text{KCI})}}{S_{\text{TICI}(\text{NaCI})}} = \frac{S_{\text{TIX}}(\text{KX})}{S_{\text{TIX}}(\text{NaX})} = \frac{S_{\text{TIY}}(\text{KY})}{S_{\text{TIY}}(\text{NaY})} = \dots$$
 (26)

where X, Y....represent various anions. This equation, however, is clearly erroneous.

This is indicated, for instance, by the fact that oxalotetrammine-cobaltic chloride and nitrate give the following values for  $0.1\ N$  solution of the solvents.

$$\frac{s_{\text{OxCl(KCl)}}}{s_{\text{OxCl(NaCl)}}} = 1.020 \qquad \frac{s_{\text{OxNO3(KNO3)}}}{s_{\text{OxNO3(NaNO3)}}} = 1.051$$

and chloropentammine-cobaltic chloride and nitrate,

$$\frac{SP_{Cl_2(KCl)}}{SP_{Cl_2(NaCl)}} = 1.029 \qquad \frac{SP_{(NO_2)_2(KNO_2)}}{SP_{(NO_2)_2(NaNO_2)}} = 1.092$$

These values differ widely. Similar results have been found in this Laboratory in a number of cases. The principle in question is thus clearly seen to be inconsistent with experimental facts.

Moreover, if the change of the activity coefficient of a cation, when passing from a NaX solution into a KX solution of the same strength, should be independent of the nature of X while the activity of X keeps its activity coefficient unchanged, then, as can be easily shown thermodynamically, the difference in osmotic coefficients, and therefore in freezing points, of the NaX and KX solutions should be the same independently of X; or, generally, the difference in freezing points of two salt solutions with a common ion should be independent of the nature of that common ion. This result, too, is in conflict with experimental facts. For 0.1 N solutions, for instance, we have the following markedly varying differences in the molar freezing-point lowerings,  $\Delta_1 - \Delta_2$ .

Saltı	Salt	$\Delta_1 - \Delta_2$	Difference
NaNO ₃	KNO ₃	0.090 \	0.002
NaCl	KCI	.027	0.063
KC1	KNO ₃	.148	000
NaCl	NaNO ₃	.085	.063

It would be of no assistance to make the high concentrations in the above examples responsible for the failure of the principle, because this carries meaning only if the deviations from it are small, compared with the

deviations from the ideal values generally exhibited by the ions. Decrease in concentration would, therefore, mean no improvement in applicability.

The principle of independent activity coefficients, whether taken in the sense of Lewis and Randall,⁷ or as the modification proposed by Harned and Brumbaugh, is thus clearly seen to fail in accounting for the individual properties of salt solutions. It can be stated as a general and obvious conclusion that the thermodynamic and experimental evidence which has been found to be strongly confirmatory of the principle of the specific interaction of ions at the same time excludes the possibility of describing the phenomena in question by means of any theory in which "independent" activity coefficients are involved, since it is the most marked feature of this principle that the activity coefficient of an ion is, to a similar extent, a function of the nature of the ion itself and of the nature of the solution containing it.⁸

## Experimental Part. Solubility of Cobalt Ammonia Salts in Sodium Sulfate and Sodium Chloride Solutions⁹

Only uni-univalent salts were used for solvents in the earlier experimental verification of the principle of the specific interaction. As it would be of interest to try to broaden the experimental basis of the principle, experiments were performed in which solutions of sodium sulfate and chloride were used as solvents. The dissolving powers of these two solvents differ by a greater amount than in the case of two uni-univalent salt solutions and a more rigid verification is, therefore, possible with them.

As saturating substances the following three uni-univalent cobalt salts were employed: (1) oxalotetramminecobaltic-tetrathiocyanato-diammine chromiate,  $[Co(NH_3)_4Ox][Cr(NH_3)_2(CNS)_4] = OxR$ ; (2) oxalotetramminecobaltic-oxalodinitrodiammine cobaltiate,  $[Co(NH_3)_4Ox][Co(NH_3)_2(NO_2)_2Ox] = OxN$ ; (3) nitrothiocyanato-tetramminecobaltic-oxalodinitrodiammine cobaltiate,  $[Co(NH_3)_4(CNS)(NO_2)][Co(NH_3)_2(NO_2)_2Ox] = RnN$ ; of these 1 and 2 have a cation, and 2 and 3 an anion in common. Furthermore, two oxalotetrammine cobaltic salts with a bivalent anion were employed, namely, (4) oxalotetramminecobaltic persulfate,  $[Co(NH_3)_4Ox]_2S_2O_8 = Ox_2S_2O_8$ , and (5) oxalotetramminecobaltic dithionate,  $[Co(NH_3)_4Ox]_2S_2O_8 = Ox_2S_2O_8$ . All of these compounds are well-crystallizing salts, rather stable in solution and very slightly soluble in water. The solubility data for pure water as solvent at 20° are (1) OxR, 0.00139 M; (2) OxN, 0.000670 M; (3) RnN, 0.000449 M; (4) Ox₂S₂O₈, 0.000755 M; (5) Ox₂S₂O₆, 0.000201 M.

Table I gives the solubilities in the salt solutions, c being the equivalent

⁸ Ref. 1, p. 878.

Experiments by Kirsten Volgvartz.

concentration of the solvent solutions and s the molar solubility, using for each salt its solubility in pure water as unity.

TARLE T Solubility of OxR, OxN and RnN in Na2SO4 and NaCl Solutions at 20°

	, c	SNa2SO4	$s_{ m NaCl}$	SNacSO1
	0.005	1.086	1.040	1.040
	.01	1.143	1.071	1.068
OxR	{ .02	1.228	1.118	1.099
	.05	1.369	1.183	1.157
	( .1	1.527	1.260	1.212
	( .005	1.107	1.065	1.039
	.01	1.176	1.103	1.067
OxN	.02	1.268	1.153	1.099
	.05	1.459	1.266	1.153
	( .1	1.688	1.403	1.202
	( .005	1.071	1.060	1.010
	.01	1.111	1.090	1.016
RnN	.02	1,144	1.125	1.018
	.05	1.230	1.203	1.022
	( .1	1.307	1.272	1.028

A glance at the solubility ratios  $\left(R_I = \frac{s_{\text{Na_2SO_4}}}{s_{\text{NaCl}}}\right)$  in the last columns of

this table shows that there is very close agreement between the values for the two salts with a common cation and a very striking deviation between the values for the two salts with a common anion. This is also shown by the accompanying graph, Fig. 3, in which the solubility ratios are plotted against the concentrations of the solvents.

These facts, however, are in full conformity with the principle of the specific interaction, as seen from the following thermodynamic equations,

$$R^{2}_{OxR} = \left[\frac{S_{OxR(NacSO4)}}{S_{OxR(NacI)}}\right]^{2} = \frac{f_{Ox(NacI)} f_{R(NacI)}}{f_{Ox(NacSO4)}}$$
(27)  

$$R^{2}_{OxN} = \left[\frac{S_{OxN(NacSO4)}}{S_{OxN(NacI)}}\right]^{2} = \frac{f_{Ox(NacI)} f_{R(NacSO4)}}{f_{Ox(NacSO4)} f_{N(NacSO4)}}$$
(28)  

$$R^{2}_{RnN} = \left[\frac{S_{RnN(NacSO4)}}{S_{RnN(NacI)}}\right]^{2} = \frac{f_{Rn(NacI)} f_{N(NacSO4)}}{f_{Rn(NacSO4)} f_{N(NacSO4)}}$$
(29)

$$R^{2}_{\text{RnN}} = \left[ \frac{s_{\text{RnN} (\text{NacSO4})}}{s_{\text{RnN} (\text{NacI})}} \right]^{2} = \frac{f_{\text{Rn} (\text{NacI})} f_{\text{N} (\text{NacSO4})}}{f_{\text{Rn} (\text{NacSO4})} f_{\text{N} (\text{NacSO4})}}$$
(29)

where  $s_{OxR(Na_8SO_4)}$  means the solubility of OxR in the Na₂SO₄ solution,  $f_{Ox(NaCl)}$  the activity coefficient of the Ox ion in the sodium chloride solution, etc. Now, dividing (27) by (28), and (28) by (29), we obtain

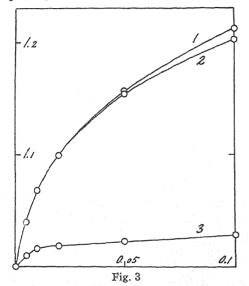
$$\left(\frac{R_{\text{OxR}}}{R_{\text{OxN}}}\right)^{2} = \frac{\frac{f_{\text{R (NaCl)}}}{f_{\text{R (NaSO4)}}}}{\frac{f_{\text{R (NaSO4)}}}{f_{\text{N (NaCl)}}}}$$

$$\left(\frac{R_{\text{OxN}}}{R_{\text{RoN}}}\right)^{2} = \frac{\frac{f_{\text{Ox(NaCl)}}}{f_{\text{N (NaSO4)}}}}{\frac{f_{\text{Ox(NaSO4)}}}{f_{\text{Rx (NaCl)}}}}$$
(31)

$$\left(\frac{R_{\text{OxN}}}{R_{\text{RnN}}}\right)^2 = \frac{f_{\text{Ox}(\text{Nac})}}{f_{\text{Ox}(\text{NacSO4})}} \frac{f_{\text{Ox}(\text{NacSO4})}}{f_{\text{Rn}(\text{NacI})}} \tag{31}$$

Since in (30) (but not in (31)) the right hand side of the equation according to our principle equals unity, the solubility ratios  $R_{\rm OxR}$  and  $R_{\rm OxN}$  but not  $R_{\rm OxN}$  and  $R_{\rm RnN}$ , accordingly, should be equal. The values in Table I furnish, therefore, a complete verification of the theory.

In an earlier communication ¹⁰ it was concluded that the solubility of uni-univalent salts was mainly governed by the equivalent concentration of the solvent, independent of its type; that is, that the shape of the solubility curves of such salts suffered no general or typical alteration when passing from one solvent to another of different type. The data now



available at low concentration show that this conclusion must be abandoned. The R-curves in the case of sodium sulfate and chloride are not rectilinear but exhibit a curvature particularly pronounced at high dilution. We infer that univalent ions are influenced by oppositely charged ions to an extent that is systematically dependent on their valence.

The values in the second and third columns of Table I confirm the earlier finding regarding the marked individualities of the activity coefficients of salts even at great dilution. It is of par-

ticular interest that the principle of the specific interaction holds in spite of very great difference in the individual values of the activity coefficients in the various solvents.

Table II

Solubilities of OxR and OxN in Solutions of Sodium Sulfate and Sodium

Chloride of High Concentrations at 20°

	с	SNa2804	SNaCl	SNa2SO4 SNaCl
	$\left(0.1\right)$	1.527	1.260	1.212
OxR	0.2	1.719	1.367	1.256
Oxx	0.5	1.957	1.525	1.283
	1.0	1.993	1.626	1.224
	0.1	1.688	1.403	1.202
OxN	0.2	2.000	1.612	1.239
OXIV	0.5	2.657	2.149	1.238
	(1.0	3.448	3.060	1.130

¹⁶ Brönsted and Petersen, This Journal, 43, 2280 (1921).

The principle of the specific interaction may be expected to hold true only in dilute solution. Some measurements were made with the two oxalotetrammine salts at higher concentrations in order to determine the limits for its validity. The results are recorded in Table II.

The deviations from the principle, as exhibited by the values of  $\frac{S_{\text{Na;SO}_4}}{S_{\text{Na;Cl}}}$  for the two salts at equal concentrations of the solvents, are perceptible in 0.1 N solution and very pronounced at higher concentrations.

The results obtained with two uni-bivalent salts in dilute solutions are given in Table III, the same notation being used as above.

Table III Solubilities of  $\rm Ox_2P$  and  $\rm Ox_2D$  in Solutions of Sodium Sulfate and Sodium Chloride at  $20\,^\circ$ 

	c	SNazSO4	SNaCl	SNa2SO4
	•	-11111004	-11401	SNaCl
	0.01	1.259	1.157	1.087
0 0 0	.02	1.409	1.250	1.126
$Ox_2S_2O_8$	.05	1.743	1.445	1.199
	.1	2.175	1.716	1.269
	.01	1.292	1.185	1.091
0-20	.02	1.465	1.294	1.133
$Ox_2S_2O_6$	.05	1.850	1.53	1.208
	.1	2.27	1.81	1.284

The values in the last column of this table show that the solubility ratios  $\left(R_{II} = \frac{s_{\text{Na;SO}_4}}{s_{\text{Na;Cl}}}\right)$  in this case also are nearly identical for the two salts at the same concentrations of the solvents, as expected from our theory.

If the ratio of the solubilities of a salt in the two solvents is taken not at the same equivalent concentration as in all the above calculations, but at the same molar concentration or at the same ionic strength¹¹ this ratio will generally approach much closer to unity. When plotting the solubilities against the ionic strength, the curves tend to coincide at very low

concentrations. The identity of the values of  $\frac{s_{\text{Na:SO}_4}}{s_{\text{NaCl}}}$  found by com-

paring two isotypic salts with a common cation does, however, appear only when the equivalent concentration is used, that is, when the cation of the solvent is present in the same concentration in the two solutions compared, a fact which is in full conformity with the ideas underlying the principle of the specific interaction of ions.

Since the measurements here mentioned involve saturating salts of different type, but with an ion in common, the salting-out ratio,  $r_u = \frac{f_{\text{(CI)}}}{f_{\text{(SO)}}}$ , can be calculated according to the theory given in the previous ¹¹ Ref. 8, p. 1140.

article.¹² Applying the formula derived there  $r_u = R_I^4/R_{II}^3$  and introducing the values of  $R_I = Rox_N$  and  $R_{II} = Rox_2 s_2 o_6$  from the tables, we find the values of  $r_u$  corresponding to the concentrations c as follows,

G	0.01	0.02	0.05	0.10
Tu	1.019	0.997	0.998	1.013

that is to say, values very near unity. As far as these experiments are concerned, the salting-out effects of the two solvents are then very nearly identical.

#### Summary

- 1. The principle of the specific interaction of ions is presented in the form of a simple equation and a diagram.
- 2. The individualities of the thermodynamic properties of salts vary linearly with their concentration when the total concentration is kept constant. On the basis of this law several of the results obtained by means of the principle of the specific interaction may be derived.
- 3. Thermodynamic and experimental evidence to prove the invalidity of the principle of the independent activity coefficients has been adduced.
- 4. Solubility measurements embracing a series of cobaltic ammonia salts in solutions of sodium sulfate and sodium chloride have been carried out. The results were found in full agreement with the principle of the specific interaction.

COPENHAGEN, DENMARK

[Contribution from the Laboratory of Physical Chemistry of the University of Wisconsin]

# DETERMINATION OF SIZE AND DISTRIBUTION OF SIZE OF PARTICLE BY CENTRIFUGAL METHODS

By The Svedberg and J. Burton Nichols Received September 14, 1923

In the determination of size and distribution of size of particle through gravity sedimentation by Odén's method¹ one is limited to relatively coarsely grained sols of about  $100~\mu\mu$  radius or larger. Since this is due to the extremely slow rate of settling, if the effect of gravity be increased sols of true colloidal size might thus be determined. To this end we have employed centrifugal force, and since direct weighing becomes impracticable here we designed a special centrifuge so constructed that the sol may be observed as it is precipitated. Then for a uniform sol, size of particle may be determined by measuring the rate of movement outward of the boundary of the particles and applying a modified form of Stokes' law.

¹² Ref. 1, p. 885.

¹ Odén, Bull. Geol. Inst. Upsala, 16, 15 (1918).

With the centrifuge the acceleration of the particle is no longer constant as in the case of gravity sedimentation but varies with the distance from the center.

Let a be the distance from the axis of rotation to the meniscus of the sol in the centrifuge tube. Then let x be the distance the boundary of the particles has moved in a given time t. Now consider the forces acting on a particle at the point x. The frictional force which tends to cause it to resist movement is  $6\pi\eta r(\mathrm{d}x/\mathrm{d}t)$  where  $\eta$  is the viscosity of the liquid, r the radius of the particle considered to be a sphere, and  $\mathrm{d}x/\mathrm{d}t$  its velocity. But the centrifugal force applied to cause movement is  $4/3\pi r^3(d_p-d_l)-w^2(x+a)$ ,  $(d_p-d_l)$  being the difference in density between the particles and dispersion medium, w the angular velocity, and (x+a) the distance from the axis of rotation to the particle.

Equating and rearranging for integration

$$\int_{0}^{t} r^{2} dt = \int_{0}^{x} \frac{9\eta}{2 (d_{x} - d_{l}) \quad w^{2}} \frac{dx}{x + a}$$

$$r^{2} t = \frac{9\eta}{2 (d_{y} - d_{l}) \quad w^{2}} ln \left(\frac{x + a}{a}\right)$$

$$r = \sqrt{\frac{9\eta ln \left(\frac{x + a}{a}\right)}{2 (d_{y} - d_{l}) \quad w^{2}t}}$$
(1)

Therefore, by measuring the distance x which the boundary of the sol has moved out in a time t, and obtaining the speed of the centrifuge it is possible to determine r.

Fig. 1 shows the centrifuge devised. The rotor A is directly connected at B to a Dumore special 20,000 r.p.m. motor C suspended in the heavy metal casing D and supported by a pivot bearing E. The machine is mounted on a large wooden base F, laminated to prevent warping, and several thicknesses of linoleum are glued on the top and bottom to absorb vibration.

The rotor is enclosed in a square metal box G for the purpose of protecting the tube from air currents and resulting temperature differences. Air may be blown through the box also in order to obtain constant temperature. The top is made removable so that the rotor may be adjusted when necessary.

The rotor consists of the central head H, horizontally cored I, to which are screwed the two arms J, also cored to correspond to the core of the head. These arms are closed at the outer end by screw caps K to provide a means for changing the tubes L contained. In order to obtain vertical or horizontal illumination of the tubes, the arms are slotted M, top and bottom and on both sides.

The tubes used L, one for each arm, are made of a good resistance glass tubing such as Pyrex or Jena, sealed off smoothly at the outer end and closed at the inner end by paraffined corks. To prevent too much strain on the rounded portion a plastic substance is filled in the space between the tube and the cap K.

A thin metal disk N, of slightly greater diameter than the length of the rotor, attached to the head just below the arms, is slotted at O directly under the vertical slots in the arms and is fixed in position so that no relative motion of arms and disc will take place. This slotted disk therefore allows light to travel up through the box only when an arm is directly over the narrow beam of light employed for illumination.

Underneath the box is mounted a narrow plane mirror P for directing a uniform beam of light vertically through a slot Q in the bottom of the box, of the same length as the slots in the arms, so that every time an arm passes over this slot a beam of light

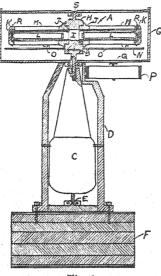


Fig. 1

travels up through the slots in the arm and through a corresponding slot in the top of the box, where the image of the contents of the tube may be observed or photographed. There is also a slot in the side of the box at such a height that light reflected from the contents of the tubes also may be viewed or photographed.

The most difficult problem to solve was to provide a good means of balancing the rotor. This is essential, for when it is not in exact balance the vibrations tend to mix the colloid and vitiate the effect of the force applied. Several different methods were employed but none was sensitive enough. However, the desired sensitivity was finally obtained by inserting a hardened steel peg on each side of the head, in order to furnish a means of support for the rotor on knife edges. These rods are so situated that the center of gravity of the rotor lies

just below the point of support, such arrangement giving maximum sensitivity. Then the end of each arm was threaded and adjustable rings R

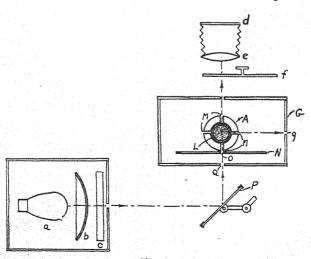


Fig. 2

gave us the means for varying the movement of the arms so that they would come to rest in a horizontal position.

Fig. 2 gives a diagrammatic representation of the apparatus and the path of the beam of light up through the sol in the centrifuge tube to the photographic plate. In this case the section of the centrifuge box is at right angles to the view shown in Fig. 1.

The source of light is a concentrated filament electric light bulb a;b is a lens of white glass to make the light beam of uniform color and intensity; c is a water cell for cooling the beam. This system is entirely enclosed in a large, asbestos-lined box to shut out stray light from the camera lens. The light then travels through a slot in the side of the

box to the narrow plane mirror P mentioned before, which reflects it up into the centrifuge box through the slot Q. Now if the arm is directly over this slot the beam of light can continue up through the slot O in the disc screen and through the slots M in the arms and out at the top slot in the box where the image of the illuminated tube containing the sol is thrown on the photographic plate d, by the large lens e; f is a sector wheel rotated at a constant rate by a small motor so as to give a known length of time of exposure to the plate.

If it is desired to photograph the reflected light from the colloid rather than the transmitted light, the camera arrangement may be changed to a horizontal position in front of the slot g. In this arrangement another light system of equal intensity to that shown is introduced so that both the bottom and the top side of the tube can be equally lighted.

Speed regulation is provided for by inserting a variable resistance in the field circuit of the motor. In this way any desired speed may be obtained. Speed of the machine is determined by inserting a speed counter or indicating tachometer at S, the top of the axis of rotation (Fig. 1).

#### Uniform Sols

The first material studied was two gold hydrosols prepared by means of Zsigmondy's nuclear method.

Equal amounts of one of the sols were sealed in centrifuge tubes and placed in the rotor of the machine. The centrifuge was started, the resistance adjusted to give the desired speed and the time of starting noted when the centrifuge had come up to speed. After a certain length of time

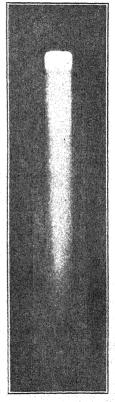


Fig. 3

the distance the boundary had moved was measured either directly by means of a centimeter scale on a glass slide or else by photographing the tube and measuring the distance from the meniscus of the sol to the boundary of the particles. The latter procedure is necessary when the boundary is not sharp. In order to get the correct point the gradual increase in density of the plate in this region was measured with a König Martin photometer and the point of medium density was considered to be the edge of the boundary; then by taking another photograph later and determining

the point on the picture corresponding to the same density the true distance moved in the given time interval could be determined.

Fig. 3 indicates the appearance of the photograph obtained. The particular photograph shown is of gold sol No. 2 at the end of 30 minutes of centrifuging.

In order to verify the values obtained from the runs with the centrifuge, the sols were determined directly by means of the ultramicroscope.

Table I
Data on Gold Hydrosol Number 1

$$r = \sqrt{\frac{9\eta \ln \frac{x+a}{a}}{2(d_p - d_1) \quad w^2 t}}$$

where a= distance from axis of rotation to meniscus of sol, 2.7 cm.; t= time of centrifuging in minutes; x= distance sedimented in cm.; r= radius in  $\mu\mu$ ;  $\eta=$  viscosity, 0.01; w= angular velocity,  $60\pi$ ;  $d_p-d_l=$  difference in density, 18.32.

Min.	Z Cm.	γ μμ	r (from ultramicroscope determination) μμ
10	0.15	24.1	
20	.28	21.1	
			21.8
30	.42	20.9	

TABLE II

Data on Gold Hydrosol Number 2  $a=2.0~{\rm cm}; \eta=0.01; d_p-d_l=18.32; w=58\pi$ 

t Min.	x Cm.	γ μμ	r (from ultramicroscope determination) μμ
15	0.3	34.0	
30	.7	35.1	
			33.5
47	.9	32.6	

In each case, considering the last value obtained with the centrifuge as the best, the results by the two methods are seen to be in very close agreement.

A sample of colloidal barium sulfate was next studied. This was made by the interaction of  $0.1\ N$  barium thiocyanate with  $0.1\ N$  ammonium sulfate, using potassium citrate as a protective agent.

Table III Barium Sulfate

 $a = 2.4 \text{ cm.}; \eta = 0.01; w = 31\pi; d_p - d_l = 3.4$ r (from ultramicroscope 12 determination) Min.  $\mu\mu$  $\mu\mu$ μμ 60 0.3 1.4 67.7142.2105 .7 5.575.3154.5 93.3 135 6.6 74.0151.0

With the barium sulfate used a very sharp boundary was obtained representing the larger size of particle, probably indicating a steep maximum at this point, and a fainter boundary representing the minimum size of particle present. As might be expected with two such very differently sized particles, the ultramicroscopic determination representing the average size of particle gives us very little information here. In addition, the barium sulfate particles scatter very little light, so the counts are difficult to make with the ultramicroscope.

The next material studied was a sample of Putnam clay prepared by Professor Bradfield of the University of Missouri. This contained a fairly narrow range of size of particle, since it represented that fraction obtained on passing the clay through a Sharples centrifuge at a speed of 30,000 r.p.m., collecting a 3-minute fraction and then passing this fraction through again and collecting the particles thrown out in three minutes.

The following results were obtained.

TABLE IV CLAY  $a = 2.5 \text{ cm.}; \eta = 0.01; w = 58\pi; d_p - d_l = 1.6$ r (from ultramicroscope determination) Min.  $\mu\mu$ 60 0.2 43.3 90 .3 42.149.4 135 41.7 .45 345 1.15 39.4

Since a slight error in measurement of the larger distance does not introduce so great an error in the results, the lower value of r obtained in the centrifuge run probably represents the minimum size of particle present. In the ultramicroscopic determination the particles were difficult to distinguish, as similar to the barium sulfate, they scatter very little light.

A sol of arsenious sulfide prepared by passing hydrogen sulfide into a solution of arsenic trioxide was also studied. As in the case of the sol of barium sulfate a double boundary appeared, the outer one being very sharp, while the inner was rather faint and indistinct.

TABLE V ARSENIC TRISULFIDE SOL  $a = 2.7 \text{ cm.}; \eta = 0.01; w = 58\pi; d_p - d_l = 2.46$ r (from ultramicroscope determination) 71 Čm. Cm. Min. μμ μμ LLIL 62.3 75.50.2 0.3 17 74.030 .4 .55 65.275.5.8 63.9 73.7.6

It should be noted that with non-spherical particles such as those of barium sulfate, arsenious sulfide, and clay the values of r determined do not represent the actual radius but the equivalent radius of a spherical particle of the material that would sediment at the same rate as the actual particle.

#### Non-Uniform Sols

Since most colloidal material contains a wide range of sizes of particles, the method just described for observing the movement of the boundary can give us complete information on only a few substances or at most the smallest size of particles contained in a non-uniform sol.

Therefore the next problem is to work out the method for determining the relative amounts present of each size of particle in a sol. One of  $us^2$  has already developed the theory of the method, using an approximate formula for r. The following is more exact.

In a thin layer dx of a sedimenting sol the change in concentration dc from the section at x to the section x + dx is due to particle with radius r to r + dr, the values of r being determined from the modified form of Stokes' law, Equation 1. By obtaining the change in c with x, that is dc/dx, we may determine the distribution function  $\frac{dc}{dr} = \frac{dc}{dx} \cdot \frac{dx}{dr}$ . In order to measure dx/dr let us rearrange Equation 1 to the form

$$\ln \frac{x+a}{a} = \frac{2 (d_p - d_l) \quad w^2 t \, r^2}{9\eta}$$
Let  $B = \sqrt{\frac{9\eta}{2(d_p - d_l) \quad w^2 t}}$ 

Substituting and differentiating,

$$\frac{\mathrm{d}x}{x+a} = \frac{2r\,\mathrm{d}\,r}{B^2}$$

Substituting the value of r from Equation 1 and rearranging,

$$\frac{\mathrm{d}x}{\mathrm{d}r} = \frac{2(x+a)\sqrt{\ln\frac{x+a}{a}}}{B}$$

a being again the distance from the axis of rotation to the point x = 0. This then gives

$$\frac{\mathrm{d}c}{\mathrm{d}r} = \frac{2(x+a)\sqrt{\ln\frac{x+a}{a}}}{B}\frac{\mathrm{d}c}{\mathrm{d}x} \tag{2}$$

The following procedure is necessary in order to obtain the variation in concentration with distance x in the centrifuge tubes. First, a picture is taken of the contents of the centrifuge tube when the rotor has just come up to speed and practically no sedimentation has taken place. Then a photograph is taken on the same plate after a given length of time of running and a third photograph is taken of a wedge cell of the material. All

² Svedberg and Rinde, This Journal, 45, 943 (1923).

three pictures must be given the same intensity of illumination and length of exposure.

Then by comparing the second and the third strips in a photometer, we obtain the density on the wedge cell strip corresponding to the density of the sol representing its original concentration. Beer's law may then be used to determine the concentration at each layer of the wedge cell and the values obtained put in the form of a scale parallel to the photograph strip of the wedge cell. The density of this strip is next determined throughout the whole height which gives us concentration in terms of density. However, if the material under observation contains a wide range of sizes of particles, the variation of the light absorption constant with radius must be considered, as already pointed out by one of us.²

Finally, the density of each layer of the sedimenting sol may be obtained from the photograph taken of the contents of the tube after the centrifuge had been running for some time, and when what each density represents in terms of concentration is known, the change in concentration with distance, dc/dx, may be determined for the material. Now the distribution curve may be plotted using as coördinates dc/dr and r.

Investigations on non-uniform colloids are being undertaken and will form the subject of a later paper.

# Summary

- 1. Stokes' law has been modified to give an exact formula for determining the radius of a particle sedimenting under centrifugal force.
- 2. A special type of centrifuge has been described which permits a sol to be observed or photographed while it is being precipitated.
- 3. This method depends on the projection of a uniform beam of light up through the tube containing the material each time the tube passes over a certain point. The rate of movement of the particles in the tube may then be observed.
- 4. To illustrate the method for a fairly uniformly sized colloid, results for two different gold sols, clay, barium sulfate, and arsenious sulfide have been given.
- 5. Another method has been discussed for determining the distribution of size of particles, depending on the variation of concentration with distance from the axis of rotation in a disperse system subjected to centrifugal force.

MADISON, WISCONSIN

[Contribution from the Fixed Nitrogen Research Laboratory, United States Department of Agriculture]

# THE AMMONIA EQUILIBRIUM

By A. T. Larson and R. L. Dodge¹

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The first determination of the ammonia equilibrium was made by Haber and van Oordt² in 1905. In this investigation the reaction was studied at 1000° and 1 atmosphere pressure. In 1907 Haber and Le Rossignol³ published results of experiments which they had made at 1 atmosphere pressure and at temperatures ranging from 700° to 1000°. About this same time papers by Nernst⁴ and Jost⁵ appeared in which approximately this same temperature range was covered, but the pressure range was extended to 72 atmospheres. The following year Haber and Le Rossignol⁶ studied the ammonia equilibrium at 30 atmospheres, covering a temperature range essentially the same as that of their earlier report. The most recent work on the ammonia equilibrium appeared in 1914-1915 when Haber⁷ published a series of papers in which he gave the results of a redetermination of the equilibrium at 30 atmospheres. In the latter experiments an attempt was made to reach temperatures as low as 450° but without success, 561° apparently being the lowest temperature at which equilibrium could be established.

Using results obtained at a pressure of 30 atmospheres and temperatures ranging from 974° to 561° Haber computed the probable equilibrium values for the pressure range of 1 to 200 atmospheres and temperatures as low as 200°. These computations were based on the van't Hoff isochore, the integration of which required a knowledge of the variation with temperature of the heat of formation of ammonia from its elements. This heat of formation Haber determined experimentally.

In computing the equilibrium values for the ammonia reaction, Haber recognized the danger of applying his formula to a wide range of pressures. For the lower pressures it was felt that the effect of the deviations of the compressed gases from the perfect gas law would be negligible. At relatively high temperatures (915°) Jost⁵ has shown this to be the case.

- ¹ Assisted by L. A. Stengel.
- ² Haber and van Oordt, Z. anorg. Chem., 43, 111 (1905).
- ³ Haber and Le Rossignol, Ber., 40, 2144 (1907).
- ⁴ Nernst, Z. Elektrochem., 13, 521 (1907).
- ⁵ Jost, Z. anorg. Chem., 57, 415 (1908).
- ⁶ Haber and Le Rossignol, Z. Elektrochem., 14, 181 (1908).
- ⁷ I. Haber, Z. Elektrochem., 20, 597 (1914). II. Haber, Tamaru and Ponnaz, ibid., 21, 89 (1915). III. Haber and Maschke, ibid., 21, 128 (1915). IV. Haber and Tamaru, ibid., 21, 191 (1915). V. Haber, Tamaru and Oeholm, ibid., 21, 206 (1915). VI. Haber and Tamaru, ibid., 21, 228 (1915). VII. Haber and Greenwood, ibid., 21, 241 (1915).

Just what the effect would be at lower temperatures, say below 500° was, however, not known. Since the ammonia equilibrium had not been determined over a wide range of pressures, and particularly at the low temperatures now possible, it has been considered worth while to make such an investigation. The equilibrium results which have been obtained at 10, 30, 50 and 100 atmospheres' pressure are given in this paper.

# Experimental Part

The experimental procedure of this investigation was essentially as follows. A mixture of nitrogen and hydrogen (1:3) at 100 atmospheres was purified and then passed through a catalyst bomb in which any desired percentage of the gas could be converted into ammonia. If an ammonia-free gas was desired, the catalyst bomb was by-passed. When pressures lower than that of the purification train (100 atmospheres) were being investigated, an automatic reducing valve served to effect the reduction of the pressure to the desired value.

The gas now passed through a coiled iron pipe containing the catalyst. The catalyst was prepared by reducing iron oxide containing potassium oxide and aluminum oxide as promoters. (A detailed description of this type of catalyst will be published in a later paper.) A needle valve placed at the exit end of the coiled iron pipe was employed in regulating the flow of gas through the apparatus. This valve was provided with an electric heater which prevented condensation of ammonia at this point. After leaving this valve the gas pressure was reduced to atmospheric and the gas was then passed through a friction tube flowmeter. The equilibrium was approached from both sides, in every case the space velocity being progressively decreased until further reduction in flow produced no change in ammonia conversion.

# Preparation and Storage of Gas

The nitrogen-hydrogen mixture was prepared by burning electrolytic hydrogen and air in such proportions that the resulting gas mixture contained approximately 75% by volume of hydrogen. The remaining 25% was essentially a mixture of nitrogen and argon, the latter forming about 0.3% by volume of the total mixture. The flow of the hydrogen and the air was automatically controlled so that a gas of uniform composition was practically insured. The freshly prepared gas mixture was led into a (14 cu. meter) water-sealed gas holder, from which samples were withdrawn and analyzed by the explosion method. After the gas had been analyzed it was compressed into a storage system (200 atmospheres) which held about 113 cu. meters of gas (N.T.P.).

Analyses covering a period of 117 days gave as the average composition of the gas, 76.2% of hydrogen and 23.8% of nitrogen plus inert gas. The maximum deviation for the hydrogen was 2.2%. The volume of gas in

the high-pressure storage was about eight times the daily production, so that daily variations in the composition of the freshly prepared gas mixture were largely smoothed out. The average of the daily analyses represented with sufficient accuracy (see discussion of errors) the composition of the gas employed in these equilibrium experiments.

#### Gas Purification

Purification of the gas was accomplished by first bringing it into contact with copper at 300–400°. Here the oxygen was removed by conversion to water. The gas was then passed over a nickel catalyst maintained at 250–300°, where carbon monoxide combined with hydrogen to form methane and water. The gas was then passed through a water-cooled condenser, a tower containing soda-lime, two towers filled with porous granular alumina and finally a single tower containing fused potassium hydroxide.8

The purity of the gas was tested at regular intervals by slowly passing about 15 liters through a glass coil immersed in liquid air. No trace of condensable impurities was ever observed. An additional check on the gas purity was obtained by operating continuously a pilot catalyst whose efficiency would soon drop if a catalyst poison appeared in the gas.

#### Pressure Control

The pure gas under 100 atmospheres' pressures was reduced to any desired pressure by means of an automatic reducing valve. A pilot gage was placed in the line and served to indicate fluctuations in pressure, while the actual pressure was measured by means of an oil float (deadweight) gage, which had been checked against a similar gage calibrated by the Bureau of Standards. By means of this arrangement the desired pressures could be accurately maintained to within  $\pm 0.034$  atmosphere.

# Temperature Control

The catalyst was placed in an iron tube (length, 493 cm.; o. d., 1.72 cm.; i. d., 0.95 cm.) wound in an open coil. This coil was placed in a thermostat filled with fused sodium nitrate-potassium nitrate (1-1), the essential details of which are indicated in Fig. 1. The thermostat was made from a section of iron pipe (21 cm. in diameter and 46 cm. in length) with a welded-on bottom. Nichrome ribbon was wound on the outside of this pipe and served to maintain the fused salt mixture at approximately the desired temperature. The close regulation of the temperature was accomplished by means of a second heater (not shown in Fig. 1), immersed in the salt bath. The flow of current through this heater was controlled by means of a platinum resistance thermometer placed in the bath and

⁸ Tour, Chem. Met. Eng., 26, 588 (1922).

^o Larson and Karrer, J. Ind. Eng. Chem., 14, 1012 (1922).

connected to a Wheatstone bridge and contact galvanometer. With this arrangement the temperature fluctuations did not exceed  $\pm 0.25^{\circ}$ .

Alumel-chromel thermocouples were placed at different levels in the thermostat, the locations of two of them being indicated in Fig. 1. These couples were frequently checked either at the boiling point of sulfur¹⁰ or by direct comparison with a platinum-platinumrhodium couple calibrated by the Bureau of Standards. The bath was stirred at such a

rate that a further increase did not have any effect on the temperature uniformity.

# Analysis of Gas Sample

The ammonia content of the gas was determined by passing the gas through an absorber and collecting the nitrogen-hydrogen residue in a compensating buret. ¹¹ Samples of gas were analyzed under each condition of temperature, pressure and gas flow until three or more consecutive samples taken at intervals of from 5 to 15 minutes showed deviations of less than 1% of their

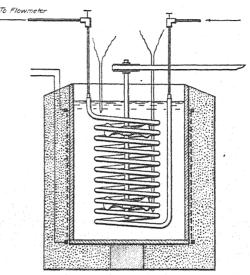


Fig. 1.—Fused salt bath

value. The average of these last samples was taken as the value for the ammonia content of the equilibrium gas mixture.

The ammonia was determined in two ways, both of which gave concordant results. In one of these methods the ammonia was absorbed in 4% boric acid solution containing either methyl orange or bromophenol blue (tetrabromo-phenolsulfonephthalein) as indicator, the ammonia being titrated with  $0.1\ N$  sulfuric acid. In the other method the ammonia was absorbed in  $0.1\ N$  sulfuric acid with sodium alizarin-sulfonate as indicator, the quantity of acid being slightly less than that required for neutralization of all the ammonia, and the excess of ammonia titrated with additional  $0.1\ N$  sulfuric acid. The sulfuric acid absorbent with sodium alizarin-sulfonate as indicator was generally used because of the particularly sharp end-point. Less than  $0.05\ cc.$  of  $0.1\ N$  sulfuric acid gave a decided color change. Its disadvantage lies in the necessity of knowing in advance approximately the amount of ammonia in the sample in order to

¹⁰ See U. S. Bur. Standards, Bull., 170 (1921).

¹¹ Tour, Chem. Met. Eng., 23, 1104 (1920).

determine approximately the correct amount of acid required for the sample. The efficiency of the absorption was tested by using two absorption bottles in series but no titrable amounts of ammonia were ever found in the second bottle.

#### Gas Flow

The rate of flow of gas passing through the catalyst coil was measured by dropping the pressure of the gas to atmospheric and passing it through a friction tube flowmeter. The flow was progressively decreased until the ammonia content of the gas leaving the catalyst coil became constant. When this occurred it was assumed that equilibrium had been reached.

With the most active catalyst available, equilibrium is not reached, particularly at the higher pressures, when the space velocity is in excess of

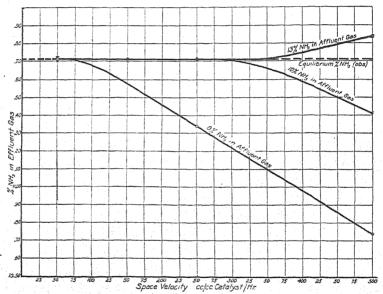


Fig. 2.—Pressure, 50 atm. (abs.) Temperature, 425°. Equilibrium, % NH3 (obs.) 11.71

5000, and the temperature is lower than 450°. For example, at 50 atmospheres' pressure and 350° equilibrium was not reached until the space velocity was lowered to 10. With 1 cc. of catalyst for example, this would give only 0.167 cc. of gas per minute, a flow which is difficult to regulate closely. Furthermore, at such a low rate of flow analyzable samples of gas cannot be withdrawn in a reasonable length of time. Under the conditions just specified, it would require 10 hours to remove a 100cc. sample. It was necessary, therefore, to use a relatively large volume of catalyst. Accordingly, about 0.5 liter of catalyst was used (484 cc.); this permitted a gas flow which was easily controllable even at the lowest space velocities

employed, and allowed the rapid withdrawal of a sample sufficiently large for analysis.

In order that the experiment might not consume too much time the gas mixture was brought very nearly to the equilibrium condition before it entered the catalyst coil. With this assistance equilibrium was of course more readily attained. Fig. 2 shows the consequences of adding ammonia to the gas when the operating conditions permitted equilibrium to be reached readily on an ammonia-free gas. In this particular case not enough observations were made to determine the shape of the curve; but for our purpose these intermediate points were unnecessary. (The results of other investigations indicate that the space-velocity curves always approach equilibrium in this manner.)

#### Discussion of Errors

The accuracy of this determination depends on the validity of four assumptions and on the accuracy of five measured values. The assumptions are: (1) that equilibrium is actually attained; (2) that the equilibrium is attained at the measured pressure; (3) that the equilibrium is attained at the point at which the temperature is measured; and (4) that no change in the composition of the gas mixture occurs while the gases are passing from this point to the analytical apparatus.

- 1. In all cases, concordant results were obtained by approaching the equilibrium from both sides, a proof that equilibrium had actually been attained.
- 2. The non-existence of a pressure gradient of more than 0.068 atmospheres throughout the reaction coil was proved by measuring the pressure simultaneously at both ends under the limiting conditions of the investigation (that is, between 10 atmospheres' and 100 atmospheres' pressure and with flows ranging from 7 cc. per minute to 7 liters per minute).
- 3. The temperature was measured in a constant-temperature zone which surrounded approximately the top half of the catalyst coil. Although the temperature of this portion of the catalyst bath was uniform, there might still be an appreciable temperature gradient within the catalyst. In fact, for reactions involving the formation or decomposition of ammonia where large quantities of heat are liberated or absorbed a uniform temperature throughout the entire mass of the catalyst can be only approximated experimentally. By using a tube of relatively small diameter, the difference in temperature between the catalyst and the bath was probably not very great, even in that region where the reaction was most rapid. An inspection of the curves in Fig. 2 shows that when operating on ammonia-free gas, equilibrium was not attained until the flow of gas was decreased to a space velocity of 50. But at a space velocity of 500

we note that the reaction is approximately 90% completed. In other words, while operating at a space velocity low enough to give equilibrium (50 s. v.) 90% of the equilibrium amount of ammonia is formed in the first tenth of the catalyst. Since the catalyst filled the coil completely and the gases entered at the bottom there is no doubt that the equilibrium attained in the catalyst coil corresponds to the temperature of the bath surrounding the upper half of the catalyst coil.

4. In order to comply with the requirements of the fourth assumption a 1.6 mm. copper tube fitted with a steel adapter was pushed down to the catalyst. The copper tube was silver-soldered to the adapter and the adapter was welded to the iron pipe. (See Fig. 3.) In practice, the surface of the fused-salt bath was kept just below this soldered connection.

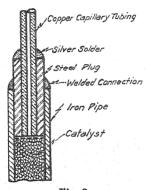


Fig. 3

In order to prevent particles of catalytic material being carried into the copper tube, a fine platinum gauze was placed between the catalyst and the copper tube. By passing the gas at a comparatively high linear velocity through a tube which has no catalytic action at these low temperatures, it is believed that there was no change in composition of the gas after it left the catalyst.

The five measured values on which the accuracy of the determination depends are (1) the composition of the gas mixture used, (2) the pressure, (3) the measurement of the residual

gas volume, (4) the titration of the ammonia absorbed from the equilibrium mixture and (5) the temperature.

- 1. In calculating the results the average composition of the gas mixture taken was 76.2% of hydrogen, 23.5% of nitrogen, 0.3% of argon. Since a 10% variation in the 3:1 hydrogen-nitrogen ratio produces an error of only 0.2% in the equilibrium constant and less than 1% in the percentage of ammonia at equilibrium, no appreciable error is introduced in employing this average value.
- 2. The pressure in the reaction coil was measured with an accuracy of 0.034 atmosphere. An error of 0.068 atmosphere at 10 atmospheres would cause only 0.7% error in the equilibrium constant; at the higher pressures the error would, of course, be correspondingly less.
- 3. The residual gas volume was measured with an accuracy of 0.2% which corresponds to an equal error in the calculation of the percentage of ammonia at equilibrium and an approximately equal error in the equilibrium constant.
- 4. The error in the standard acid solution was not greater than 0.5%. An error of 0.05 cc. in the titration of samples taken at 10 atmospheres

and  $500^{\circ}$  would cause a 1% error in the percentage of ammonia (at the lower temperatures and higher pressures the error would be correspondingly less). All the errors of analysis acting in the same direction would give an error of 1.7% in the percentage of ammonia. This corresponds to an approximately equal error in the equilibrium constant.

Table I
Observed Percentage of Ammonia at Equilibrium

Pressure (Atm ahs)					
10	30	50	100		
10.38					
7.35	17.80	25.11			
5.25	13.35	19.44	30.95		
3.85	10.09	15.11	24.91		
2.80	7.59	11.71	20.23		
2.04	5.80	9.17	16.35		
1.61	4.53	7.13	12.98		
1.20	3.48	5.58	10.40		
	10.38 7.35 5.25 3.85 2.80 2.04 1.61	10 30 10.38 7.35 17.80 5.25 13.35 3.85 10.09 2.80 7.59 2.04 5.80 1.61 4.53	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		

5. An inspection of Table I, shows that a 1° change in the temperature produces about 1% change in the percentage of ammonia at equilibrium. Since the temperature was measured with an accuracy of 0.5° the errors from this source probably do not exceed 0.5%. This would produce approximately the same percentage error in the equilibrium constant.

From the above considerations it is evident that the maximum error in the equilibrium constant might reach 3%. It is believed that the probable error, however, is very much smaller than this.

#### Results

The equilibrium percentages of ammonia obtained for the temperatures and pressures studied are given in Table I. In Table II the constant for the expression  $K_p = \frac{p_{\rm NH_2}}{p_{\rm N_2}^{1/2} \times p_{\rm H_2}^{3/2}}$  has been calculated for each of the pressure and temperature conditions indicated in Table I.

# Thermodynamic Calculations

If experimental data were available showing the volume changes which the nitrogen-hydrogen-ammonia mixture undergoes for various conditions of temperature and pressure, it might be possible with the aid of the van't Hoff equation to formulate a single expression which would satisfy the data given in Table I. By means of such a formula one would then be able to compute the equilibrium percentage of ammonia for any other temperature and pressure. Haber's formula (I) has been used for this purpose and is probably quite exact for relatively high temperatures. Jost working at 915° in Nernst's laboratory found that the pressure effect was negligible. Undoubtedly the ammonia is sufficiently "perfect" a gas at this high temperature so that the effect of pressure be-

comes negligible. At somewhat lower temperatures, however, deviations from the "perfect" gas laws undoubtedly become sufficiently great so that the pressure effect cannot be wholly ignored. The only experimental evidence for this so far presented is that by Greenwood'(VII) in Haber's laboratory who showed that the equilibrium constants in the neighborhood of 537° did vary with the pressure. Greenwood found, however, that the constant increased as the pressure is decreased, an observation which is quite the opposite of that shown in Table II. It is reasonably certain, however, that equilibrium was not reached in Greenwood's experiments, so not much importance is attached to this apparent disagreement with our result.

 $\begin{array}{c} \text{Table II} \\ \text{Observed Equilibrium Constant} \\ ^{1}/_{2}N_{2} \, \div \, ^{3}/_{2}H_{2} \, = \, NH_{3} \end{array}$ 

	76	$C_p = \frac{P \text{NH} 3}{1.5 \text{ NH} 3}$		
	4.	$p_{N_2} \sim p_{N_2} \times p_1$	H2 ³ /2	
Temp. °C.	10	Pressure	(Atm. abs.)————————————————————————————————————	100
325	0.0401			
350	.0266	0.0273	0.0278	
375	.0181	.0184	.0186	0.0202
400	.0129	.0129	.0130	.0137
425	.00919	.00919	.00932	.00987
450	.00659	.00676	.00690	.00725
475	.00516	.00515	.00513	.00532
500	.00381	.00386	.00388	.00402

Unfortunately, no data are at present available which make possible even a rough calculation of the extent to which the equilibrium constant might be expected to vary with the pressure. Whatever the pressure range covered, nitrogen and hydrogen are probably nearly "perfect" gases even at the lowest temperature studied. Although the temperatures studied by us are somewhat higher than those investigated by Roth, 12 the indications are that even at these temperatures the ammonia is still somewhat more compressible than a "perfect" gas, so that even if the magnitude of the effect cannot be predicted from present data, the effect as observed by us is certainly in the right direction.

For any given constant pressure, however, the van't Hoff equation  $\left(\frac{\partial \log K_p}{\partial T}\right)_p = \frac{Q_s}{RT^2}$  may be employed to treat the variation of the equilibrium constant,  $K_p$ , with the temperature. To integrate this expression it is first necessary to know how the heat of formation of ammonia from its elements varies with temperature. The integration constant may then be exactly evaluated from a single equilibrium determination, or approximately evaluated by means of Nernst's heat theorem. At present the heat

¹² Roth, Ann. Physik., [2] 11, 1 (1880).

of reaction and thermal properties of these gases are not known with sufficient accuracy to make possible the computation of equilibrium data by this method. Consequently, any formula which closely fits the observed data must of necessity be largely empirical.

Taking the best data available, Haber formulated the following expression based upon the reaction isochore, which he held to combine all the results of his equilibrium experiments and thermal determinations

$$\log K_p = \frac{9591}{4.571T} - \frac{4.98}{1.985} \log T - \frac{0.00046}{4.571} T + \frac{0.85 \times 10^{-6}}{4.571} T^2 + 2.10$$

This formula was largely derived from results obtained at 30 atmospheres.⁷ If we use the more recent data for the specific heats of the gases¹³  $c_{p_{\rm Hz}} = 6.50 + 0.0009 \ T$ ,  $c_{p_{\rm Nz}} = 6.50 + 0.0010 \ T$ , and  $c_{p_{\rm NHz}} = 8.04 + 0.0007 \ T + 5.1 \times 10^{-6} T^2$  and the heat of formation of ammonia at T = 0 as 9500,¹⁴ integration of the van't Hoff reaction isochore gives

$$\log \ K_{P} = \frac{9500}{4.5787T} - \frac{4.96}{1.9885} \log \ T - \frac{.000575}{4.5787} \ T + \frac{0.85 \times 10^{-6}}{4.5787} \ T^{2} + I$$

By choosing proper values for the integration constant and modifying the numerical coefficients we obtained empirical equations which fit our experimental data within the limits of experimental error. The constants and coefficients for the equations are given below. The equation has the

general form 
$$\log K_p = \frac{\alpha}{T} + \beta \log T + \gamma T + \delta T^2 + I$$
.

Pressure		150		8	
Atm.	α	β	γ	×107	I
10	+2074.8	-2.4943	0	+1.856	+1.993
30	+2074.8	-2.4943	$-3.4 \times 10^{-5}$	+1.856	+2.021
50	+2074.8	-2.4943	$-1.256 \times 10^{-4}$	+1.856	+2.090
100	+2074.8	-2.4943	$-1.256 \times 10^{-4}$	+1.856	+2.113

The observed data and those computed from these formulas are collected in Tables III and IV. For purposes of comparison we have included values computed from Haber's formula (see above). The observed results for temperatures above 500° were obtained by plotting Haber's experimental data and selecting from the curve the most probable values for the temperatures indicated.

Because of the interest attached to the Nernst heat theorem we have included in Table III values for 30 atmospheres, computed from his formula.¹⁵

In the absence of exact thermal data, calculation based on the Nernst heat theorem will, of course, give only an approximate evaluation.

¹³ Lewis and Randall "Thermodynamics," McGraw-Hill Book Co., 1923, p. 80.

¹⁴ Ref. 13, p. 557.

¹⁵ Nernst, Z. Elektrochem., 16, 101 (1910). See Also Maurer, Z. anorg. Chem., 108, 284 (1920).

TABLE III PERCENTAGE OF AMMONIA AT EQUILIBRIUM Drogoure 30 Atm ahe

A. T. LARSON AND R. L. DODGE

Temp.	Observed	F.N.R.L.a calc.	Haber calc.	Nernst cale.
200		67.56	67.57	73.21
250		47.22	49.16	54.89
300		30.25	31.76	36.15
350	17.80	17.78	18.81	21.22
400	10.09	10.15	10.72	11.67
450	5.80	5.86	6.13	6.36
500	3.48	3.49	3.62	3.62
600	(1.48)	1.39	1.43	1.31
700	(0.70)	0.68	0.66	0.55
800	( .34)	.36	.35	.27
900	( .28)	.22	.21	.14
1000	( .12)	.14	.13	.09

^a Fixed Nitrogen Research Laboratory.

TABLE IV PERCENTAGE OF AMMONIA AT EQUILIBRIUM

1								10	0 Atm. ab		
Obs.	F.N.R.L.	Haber cale.		Obs.	F.N.R.L.	ealc.		Obs.	r.N.R.L. cale.	cale.	
	50.66	51.14			74.38	73.76			81.54	80.61	
	28.34	30.57			56.33	57.44			67.24	67.40	
	14.73	16.03			39.41	40.39			52.04	52.12	
7.35	7.41	8.04		25.11	25.23	26.03			37.35	37.35	
3.85	3.85	4.12		15.11	15.27	15.86		24.91	25.12	25.13	•
2.04	2.11	2.21		9.17	9.15	9.50		16.35	16.43	16.26	
1.20	1.21	1.27		5.58	5.56	5.77		10.40	10.61	10.43	
	0.49	0.48			2.25	2.34			4.52	4.47	
	0.23	0.22			1.05	1.10			2.18	2.14	
	0.14	0.12			0.57	0.59			1.19	1.15	
	0.08	0.07			.33	.34		٠	0.70	0.68	
, 4.	0.05	0.04			.21	.22			.45	.44	
	Obs.  7.35 3.85 2.04 1.20	F.N.R.L. calc.  50.66  28.34  14.73  7.35  7.41  3.85  2.04  2.11  1.20  1.21  0.49  0.23  0.14  0.08	Obs. calc. calc 50.66 51.14 28.34 30.57 14.73 16.03 7.35 7.41 8.04 3.85 3.85 4.12 2.04 2.11 2.21 1.20 1.21 1.27 0.49 0.48 0.23 0.22 0.14 0.12 0.08 0.07	F.N.R.L. Haber calc.  50.66 51.14  28.34 30.57  14.73 16.03  7.35 7.41 8.04  3.85 3.85 4.12  2.04 2.11 2.21  1.20 1.21 1.27  0.49 0.48  0.23 0.22  0.14 0.12  0.08 0.07	F.N.R.L. Cale.       Haber cale.       Obs.          50.66       51.14           28.34       30.57           14.73       16.03          7.35       7.41       8.04       25.11         3.85       3.85       4.12       15.11         2.04       2.11       2.21       9.17         1.20       1.21       1.27       5.58          0.49       0.48           0.23       0.22           0.08       0.07	F.N.R.L. cale.         Haber cale.         Obs. cale.         F.N.R.L. cale.            50.66         51.14          74.38            28.34         30.57          56.33            14.73         16.03          39.41           7.35         7.41         8.04         25.11         25.23           3.85         3.85         4.12         15.11         15.27           2.04         2.11         2.21         9.17         9.15           1.20         1.21         1.27         5.58         5.56            0.49         0.48          2.25            0.14         0.12          0.57            0.08         0.07          33	F.N.R.I., Calc.         Haber calc.         Obs.         F.N.R.I., Calc.         Haber calc.            50.66         51.14          74.38         73.76            28.34         30.57          56.33         57.44            14.73         16.03          39.41         40.39           7.35         7.41         8.04         25.11         25.23         26.03           3.85         3.85         4.12         15.11         15.27         15.86           2.04         2.11         2.21         9.17         9.15         9.50           1.20         1.21         1.27         5.58         5.56         5.77            0.49         0.48          2.25         2.34            0.14         0.12          0.57         0.59            0.08         0.07          33         34	Cobs.         F.N.R.L. calc.         Haber calc.         Obs.         F.N.R.L. calc.         Haber calc.            50.66         51.14          74.38         73.76            28.34         30.57          56.33         57.44            14.73         16.03          39.41         40.39           7.35         7.41         8.04         25.11         25.23         26.03           3.85         3.85         4.12         15.11         15.27         15.86           2.04         2.11         2.21         9.17         9.15         9.50           1.20         1.21         1.27         5.58         5.56         5.77            0.49         0.48          2.25         2.34            0.23         0.22          1.05         1.10            0.08         0.07          33         .34	Cobs.         F.N.R.L. calc. calc. calc.         Cobs. calc. calc. calc.         Cobs. calc. calc. calc. calc.         Obs. calc.	Cobs.         F.N.R.L. calc. calc.         Cobs. calc. calc.         F.N.R.L. calc. calc. calc.         Obs. calc. calc. calc.         Obs. calc. ca	Cobs.         F.N.R.I. calc.         Haber calc.         F.N.R.I. calc.         Haber calc.         Obs.         F.N.R.I. calc.         Calc. calc.         Cobs.         F.N.R.I. calc.         Calc. calc.         Obs.         F.N.R.I. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc.         Calc. calc. calc. calc.         Calc. calc. calc. calc. calc.         Calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc. calc.

The results of this paper indicate that the computation of equilibrium values for pressures other than those actually observed cannot be made with any degree of exactness. For the present, at least, computation of

TABLE V PERCENTAGE OF AMMONIA AT EQUILIBRIUM (Calculated from Experimental Data of the F.N.R.L.)

e attache in the case of the c		Pressure (A		
Temp. °C.	10	30	50	100
200	50.66	67.56	74.38	81.54
250	28.34	47.22	56.33	67.24
300	14.73	30.25	39.41	52.04
350	7.41	17.78	25.23	37.35
400	3.85	10.15	15.27	25.12
450	2.11	5.86	9.15	16.43
500	1.21	3.49	5.56	10.61

equilibrium values for much higher pressures than those reported in this paper would, therefore, not be very exact. For any of the pressures studied however, equilibrium values for temperatures lower than those actually observed can probably be computed with considerable accuracy. Such computations have been made for temperatures down to 200°, the results of which are given in Table V.

#### Molecular Heat of Formation of Ammonia

Theoretically, it should be possible to calculate the heat of the ammonia reaction by means of the van't Hoff equation. By taking equilibrium constants for temperatures very close together and assuming that the temperature coefficient for those temperature intervals can be neglected, integration of the van't Hoff equation gives the heat of formation. Computations based on the constants in Table II have been made, the results of which are given in Table VI. For purposes of comparison we have also included the heat of formation as calculated by Haber from the heat absorbed during the "cracking" of ammonia. Since a 1% error in equilibrium constant makes an error of about 5% in the calculated heat of reaction, this method of determining thermal data cannot be considered very satisfactory. As Haber has pointed out16 thermal data obtained in this way can serve only as a check on the more direct experimental methods for reaction heats and specific heats. An inspection of Table VI will show that the attempt to formulate an expression for the heat of the reaction from these would be futile.

Table VI
Molecular Heat of Formation of Ammonia

 $Q_p = 4.5707 \frac{\log K_{p1} - \log K_{p2}}{1}$ 

			$(\overline{T_1} - \overline{T_2})$					
	emperature	Haber	Calculated		.R.L. nental data, Atm 50	. abs		
	325-350	12,425	12,206					
	350-375	12,505	12,248	12,636	12,924			
	375-400	12,590	11,779	12,283	12,386	13,373		
	400-425	12,672	12,712	12,694	12,468	12,311		
	425-450	12,751	13,340	12,342	12,099	12,376		
	450-475	12,825	10,558	11,785	12,741	13,339		
	475-500	12,896	13,903	13,138	12,801	12,888		

#### Summary

1. Equilibrium values for the reaction,  $N_2 + 3H_2 \rightleftharpoons 2NH_3$ , have been determined at 10, 30, 50 and 100 atmospheres' pressure for the temperature range of 325° to 500°.

¹⁶ Haber, "Thermodynamics of Technical Gas Reactions," Longmans, Green and Co., 1908, p. 65.

- 2. Equilibrium constants have been computed for each of the pressuretemperature conditions studied. These "constants" were found to increase with an increase in pressure.
- 3. By means of empirical formulas the percentage of ammonia at equilibrium has been calculated for a temperature range of 200–1000°, and a pressure range of 10–100 atmospheres.

WASHINGTON, D. C.

[Contribution from the Chemical Laboratory of the Johns Hopkins University]

# VAPOR PRESSURES OF LITHIUM CHLORIDE SOLUTIONS AT 20°

By B. F. Lovelace, W. H. Bahlke and J. C. W. Frazer Received September 22, 1923

This paper is a continuation of a series of studies of the vapor pressures of aqueous solutions begun by Frazer and Lovelace¹ using an accurate static method which depends upon the measurement of the difference in pressure between pure solvent and solution contained in bulbs immersed in the same accurately regulated water thermostat by means of a Rayleigh manometer. The error involved in measuring the pressure differences by this method is approximately  $0.0006 \, \mathrm{mm}$ . The measurements were made at  $20^{\circ}$  and in the concentration range from  $0.1 \, \mathrm{to} \, 1.0 \, M$ .

# Experimental Details

A detailed description of the apparatus used in this work is given by Frazer and Lovelace, ¹ and by Lovelace, Frazer and Miller. ² No change in the apparatus was made except to replace the Gaede pump with a Langmuir pump using a three-stage rotary oil pump as auxiliary.

The solutions of lithium chloride were prepared from a carefully standardized stock solution, the salt for which was purified as follows. A commercial c. p. grade of lithium chloride was dissolved in distilled water, a small amount of ammonium carbonate solution added and the mixture heated and stirred for four hours to precipitate any magnesium, calcium, barium, iron or aluminum possibly present, then filtered. The ammonium carbonate used in the preparation left no residue on sublimation. To the filtered lithium chloride solution, ammonium carbonate solution was added in slight excess and the lithium carbonate filtered off and washed thoroughly with hot water. It was then heated in a platinum dish at a sufficiently high temperature to volatilize any ammonium carbonate possibly present. The salt was then suspended in a small amount of distilled water and pure hydrochloric acid added until the solution was neutral to rosolic acid. Analyses of the solution for lithium and for chlorine checked within 0.04%.

In previous investigations the removal of dissolved air from the solutions has been quite a time-consuming operation. Tests for air in the solution or solvent were made by allowing it to come to equilibrium with a large

Frazer and Lovelace, This Journal, 36, 2439 (1914).

² Lovelace, Frazer and Miller, ibid., 38, 515 (1916).

volume of vapor above it for hours.³ The vapor was then trapped off and absorbed in phosphorus pentoxide for 20 minutes and the residual pressure measured on a McLeod gage. No solution was considered air-free unless the vapor showed a residual pressure less than 0.0001 mm. Usually the solutions had required from four to six 12-hour expansions before they were air-free. In the present investigation it was found that the air could be removed in a minimum of time, that is, one 12-hour expansion. This was accomplished by introducing the solution as nearly air-free as possible into the bulb which had been previously pumped air-free, and rapidly distilling a small portion of the solvent at the pressure of its vapor into a bulb containing phosphorus pentoxide.

In detail the method is as follows.

The solutions were made up in a flask shaped like that shown in Fig. 1. The required amount of the concentrated lithium chloride solution was introduced with a pipet

into the flask which had been weighed empty. Water sufficient to bring the solution to the desired concentration was then introduced, the level marked, and a small excess added which was later removed by boiling the solution in the flask in order to remove air. The upper tube of the flask was then constricted at the portion "a" and a clean rubber tube fixed over the end of the glass and fitted with a pinchcock. The lower limb of the flask was then cautiously heated with a Bunsen flame in order to expel from this portion of the solution as much air as possible. The flame was then applied to the sides of the flask and the solution vigorously boiled for 30 minutes or more until the level was down nearly to the mark on the flask. The pinchcock was then closed and the flame removed simultaneously, the solution allowed to cool slightly and the flask sealed off at the constriction. flask was then weighed and the weight of the solution noted, in order to determine approximately the concentration. Usually about 3 g. more water than that required for the concentration



desired was present. This excess allowed for removal of water by distillation after the solutions were in the bulbs in the bath.

The sealed flask was then fixed to a mercury reservoir as shown in Fig. 2, the tube broken at "a" by pressure of the fingers and the mercury allowed to complete the filling of the flask, the flow being regulated by a pinchcock. The tube was then fitted with a capillary filled with mercury and the tip broken at b, some of the solution being wasted to replace the mercury in the capillary. The solution was then introduced into the bath in the usual manner.⁴

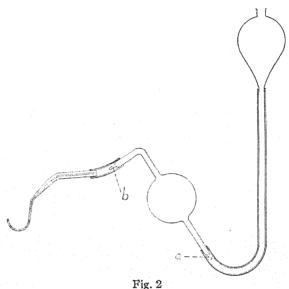
It was necessary to have the system free from air before introducing the solutions; this was accomplished quite readily by beginning the evacuation while the bulb and mercury seal were still wet. In this way a layer of water preceded the mercury up the tube leading to the bulb. The water was then removed by exposure to phosphorus pentoxide. The system was evacuated until no gain in pressure could be measured on the McLeod gage after the system had stood for 12 hours.

³ Lovelace, Frazer and Rogers, [This Journal, 42, 1794 (1920)] showed that 12 hours was necessary to establish equilibrium between solution and vapor.

⁴ Ref. 3, p. 1797.

After the solutions had been introduced into the system they were exposed to phosphorus pentoxide for a definite length of time until about 1 g. of water had been removed. It had been previously determined by experiment that the water distilled at a practically constant rate so that it was unnecessary to weigh the water removed.

The solution was then trapped off and the system evacuated to remove air given up by the solution. After distilling and evacuating the solutions thrice they were usually air-free, the whole operation requiring about 24 hours. By the method formerly used it required from four to ten days to remove the dissolved air.



In making readings of the vapor-pressure lowering, the accurate regulation of the temperature described in former articles was followed. Usually three readings of the zero point of the gage were made, three readings of the solution in the first bulb, three readings of the second solution and then two more readings of the zero. No readings were regarded as sufficiently accurate unless the zero before and after checked within 0.1 mm. scale deflection. Readings were made by two different observers extending over two or three days until four reliable sets of readings were obtained on each solution.

After the solutions were measured they were removed from the bath and placed in clean, glass-stoppered flasks and analyzed for chlorine. Concentrations (Table I) are expressed in moles of lithium chloride per 1000 g. of water.

#### Results

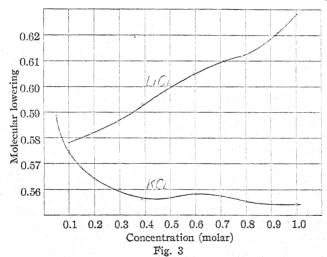
The results of the measurements are given in Table I. Col. 1 gives the room temperature, Col. 2 the concentration, Col. 3 the lowering as measured, Col. 4 the lowering corrected to millimeters of mercury at 0° and Col. 5 the lowering per mole.

The results are also shown graphically in Fig. 3 where the molecular lowering is plotted against the concentration. For comparison the data of Lovelace, Frazer and Sease⁵ on potassium chloride are shown in the same

⁵ Lovelace, Frazer and Sease, This Journal, 43, 102 (1921).

Moles LiCl per 1000 g. of water	Observed lowering Mm. Hg	Lowering corrected Mm. Hg at 0°	Molecular lowering Corrected observed lowering divided by Moles salt per 1000 g, of H ₂ O
0.0968	0.0562	0.0559	0.5775
0.1842	.1076	.1071	.5814
0.2952	.1738	.1730	. 5860
0.3862	.2300	.2290	.5929
0.4782	.2871	.2858	.5977
0.5897	.3582	.3566	.6047
0.7257	.4448	. 4428	.6101
0.7810	.4804	.4782	.6123
0.9268	.5775	. 5749	.6203
1.0316	.6518	.6489	.6290

figure. The curve for lithium chloride is considerably higher owing to the fact that this salt is highly hydrated in solution while potassium chloride is not. Although the degree of hydration decreases with increasing concen-



tration the apparent effect increases with concentration since the percentage of total solvent associated with the lithium chloride increases with the concentration.

An irregularity between 0.4 and  $0.8\,M$  similar to that found for potassium chloride⁶ is also apparent in the lithium chloride curve, but is masked somewhat in the latter case by the comparatively large slope of the curve.

In Table II the observed vapor-pressure lowerings at 20° have been compared with those calculated from the freezing-point measurements of Washburn and MacInnes.⁷ The ratio of the vapor pressure of the solution

⁶ Ref. 5, p. 106.

Washburn and MacInnes, This Journal, 33, 1701 (1911).

to that of the pure solvent at the freezing point was calculated by means of the equation⁸

$$\log \frac{N}{N+n} = \log \frac{P}{P_0} = \frac{\Delta C_P}{R} \log \frac{T_F}{T_0} \frac{-4343 (L_F - \Delta C_P \Delta T_F)}{R T_F} + \frac{0.4343 \ L F_0}{R T_{F0}}$$

where  $\frac{N}{N+n}$  is the mole fraction of solvent; P, the vapor pressure of the solution;  $P_0$ , the vapor pressure of pure solvent;  $T_F$ , the freezing point of the solution in degrees A.;  $T_0$ , the freezing point of solvent in degrees A.,  $= 273^\circ$ ;  $L_F$ , the molal heat of fusion of the solvent, = 1435.5 calories;  $\Delta C_F$ , the difference between the molal heat capacities of the solvent in liquid and solid state, = 9.05 calories;  $\Delta T_F$ , the lowering of the freezing point; R, the gas constant, = 1.985 calories.

Assuming that the ratio  $P/P_0$  is independent of the temperature the values given in Col. 3 of Table II were calculated.

		TABLE II		
Moles of LiCi		Po-		
per 1000 g. of water	$\Delta T_F$	From fp. measurements	Observed	Difference f. p.—obs.
0.1	0.351	0.054	0.056	-0.002
0.2	0.694	.115	.117	002
0.3	1.049	.178	.175	+ .003
0.4	1.416	.239	.236	+ .003
0.5	1.791	.311	.300	+ .001
0.6	2.174	.365	.365	.000
0.8	2.966	.499	. 485	+ .014
1.0	3.792	.633	.648	015

The agreement between the two is very good considering the fact that the salt is so highly hydrated in solution.

#### Summary

The lowering of the vapor pressure of water due to dissolved lithium chloride has been measured at  $20^{\circ}$  and in the concentration range of 0.1~M to 1.0~M.

An improved method for removing air from the solutions before measuring has been devised.

The observed vapor-pressure lowering has been compared with those calculated from freezing-point measurements.

BALTIMORE, MARYLAND

⁸ Mass. Inst. Tech. Quart., 21, 372 (1908).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

EQUILIBRIA IN SOLUTIONS CONTAINING MIXTURES OF SALTS¹

- III. THE SYSTEM, WATER AND THE CHLORIDES AND CARBONATES OF SODIUM AND POTASSIUM AT 25°
- IV. THE SYSTEM, WATER AND THE SULFATES AND CARBONATES OF SODIUM AND POTASSIUM AT 25°

By Walter C. Blasdale Received September 24, 1923

Although the system composed of water and the chlorides and carbonates of sodium and potassium should find important applications in dealing with the problem of separating the salts of potassium from certain brines of both natural and artificial origin, it does not appear to have been investigated. The work here reported upon is limited to a single temperature, but much information relating to the system at both higher and lower temperatures has been accumulated and will form the subject of subsequent papers. The writer is indebted to Dr. Harry East Miller for assistance in carrying out a part of the analytical work which the investigation demanded.

#### The Solid Phases Concerned

The solid phases found to be concerned in this system are the chlorides of sodium and potassium, the decahydrate, heptahydrate and five-halves hydrate of sodium carbonate, the three-halves hydrate of potassium carbonate and a hydrated double carbonate of sodium and potassium. The identification of these salts by means of the microscope formed an important part of the work here described and it was found necessary to make many preparations of them and ascertain some of their more important crystallographic and optical properties.

The difficulties encountered in preparing such hydrates free from occluded mother liquor and in drying them without loss of combined water are very great. Large crystals, whose surfaces were perfectly dry, almost invariably gave appreciable amounts of a saturated solution when crushed in an agate mortar and although smaller crystals yielded less, it was difficult to eliminate it entirely. Since the vapor tensions of most of these hydrates have not been determined, it is not possible to define with accuracy the proper conditions for drying them. The procedure usually adopted was to prepare fine crystals by rapid cooling, through a few degrees, of a saturated solution, separate these on a coarse filter as rapidly as possible, wash with solutions of alcohol of increasing concentration and allow to dry spontaneously until the odor of alcohol could no longer be recognized.

¹ The preceding articles of this series will be found in *J. Ind. Eng. Chem.*, **10**, 334 (1918) and **12**, 164 (1920).

The Decahydrate of Sodium Carbonate.—Although this hydrate is the one usually obtained at ordinary temperatures, the available data regarding its crystallography are rather meager. This is probably due to the fact that it loses water under ordinary atmospheric conditions so rapidly that accurate measurements of the interfacial angles are difficult to obtain. A limited number of such measurements were made by means of a reflecting goniometer. They showed that the crystals were monoclinic: the value found for the \beta angle was 122° 42' instead of 122° 20', as calculated by Mohs.2 Adopting the axial ratios found by him, the only planes found in the prismatic zone were (110), (100) and (010). The most conspicuous terminal planes observed were (001), (101) and (111). When the crystals were caused to separate rapidly, columnar prisms terminated by the basal plane were obtained. When they were grown more slowly, tabular forms flattened parallel to (010) and terminated by (001) and (101) were formed. Under the microscope, such crystals gave a hexagonal figure with angles of 122° 42′ (100): (001), of 115° 50′ (001): (101), and of 121° 28′ (101):(001).

The birefringence is strong and extinction is parallel to (100) and hence divides almost equally the 115° 50′ angle. The three indices of refraction reported by Larson,³ namely, 1.405, 1.425 and 1.440, do not differ sufficiently from those of the related hydrates to make identification by means of these constants certain.

The Heptahydrate of Sodium Carbonate.—The crystallography of this salt has been investigated by Rammelsberg⁴ and others. It readily forms perfect crystals of good size which assume the form of tabular prisms of easily recognizable orthorhombic symmetry. From measurements of angles in the prismatic zone, assuming the axial ratios calculated by Rammelsberg, it was found that the faces usually present were (010), (230) and (100). Similarly, it was found that the predominant terminal planes were (111) and (021). As the crystals are usually flattened parallel to the brachypinacoid the usual outline presented on the stage of the microscope was that of a 6-sided figure showing angles of 128° 40′ and 115° 40′, or of an 8-sided figure showing angles of 154° 40′ and 115° 40′, or still more rarely, of a 4-sided rectangle. The extinction is parallel to (100) and bisects the 128° 40′ angle. This serves to distinguish it from the usual forms of the decahydrate.

Under ordinary atmospheric conditions, the salt readily loses water of crystallization and when heated forms a liquid and a new solid phase, probably the monohydrate.

The Five-halves Hydrate.—This salt usually separates in the form

² Mohs, Pogg. Ann., 5, 369 (1825).

³ Larson, U. S. Geol. Survey Bull., 679, 114 (1921).

[&]quot;Hand. d. kryst. Chemie," Suppl., Leipzig, 1857, p. 75.

of needles, but occasionally as long, 4-sided or flattened 8-sided prisms, terminated by a single pair of planes intersecting at 134°. The birefringence is strong and the extinction parallel. The percentages of water found in different preparations of it were 31.04, 31.30, 32.10, 31.54, 29.90, and 30.46. Many samples contained potassium in the form of carbonate from negligible amounts to as much as 4%. The theoretical percentage of water should be 29.80 and it is believed that the variations in its composition are due to a limited amount of solid solution formation.

The Double Carbonate of Sodium and Potassium.—The formation of a double carbonate of these elements was noted by Fehling,⁵ and somewhat later by Stolba,⁶ both of whom reported a composition corresponding to NaKCO₃.6H₂O. Marguerite⁷ has also reported a salt of the composition 2Na₂CO₃.K₂CO₃.18H₂O, and still more recently, Hugounenq and Morel³ reported that the double salt which separated from solutions containing large amounts of potassium iodide varied greatly in its composition and concluded that the hexahydrates of the two carbonates formed a series of isomorphous mixtures.

Many samples obtained from solutions, which varied greatly as to the relative amounts of the two carbonates, were submitted to analysis during the course of this work. Some of these are as follows.

	A	В	C	D	Calculated (NaKCO:.6H2O)
$H_2O$	48.10	47.69	47.09	46.65	46.96
CO ₃	26.04	25.90	25.94	26.83	26.06
K	13.80	14.78	16.66	13.46	16.99

These figures seem to justify the statement that there is a certain amount of solid solution formation represented in this solid.

Perfect crystals of short columnar or tabular habit, 3 cm. in length, were easily obtained, especially when the solution contained an excess of potassium carbonate. Measurement of the more important interfacial angles of 9 well-formed crystals gave values differing but slightly from the values reported by Marignac. The most strongly developed planes were (110), (010), (100), (011), (101) and (111).

When examined on the stage of the microscope, they usually lie on the prismatic face, and in this position give an extinction angle of 25°. The indices of refraction, determined in directions parallel and perpendicular to extinction by the embedding method, were 1.428 and 1.440. When heated slowly, the salt shows a clearly defined transition temperature of 34.5°, but it is readily formed at temperatures as low as zero.

- ⁵ Fehling, Ann. Chem. Pharm., 130, 247 (1864).
- ⁶ Stolba, J. prakt. Chem., 94, 409 (1865).
- ⁷ Marguerite, Ann. Chem. Pharm., 56, 220 (1845).
- 8 Hugounenq and Morel, Compt. rend., 106, 1158 (1888).
- ⁹ Marignac, Ann. Mines, [5] 12, 55 (1857).

The Three-halves Hydrate of Potassium Carbonate.—Analyses and microscopic examination of several preparations of this salt obtained during the course of the work showed that the only hydrate formed at 25° was the three-halves hydrate.

# The Vapor and Liquid Phases

In addition to the seven solids named above, this system is concerned with a solution phase and a vapor phase composed of water vapor plus the components of the atmosphere. Variation in the composition of the liquid phase must produce corresponding variations in the partial pressure of the water vapor in equilibrium with it, and these in turn must affect the partial pressures of the oxygen, nitrogen, etc., in the vapor phase. Although these variations affect the concentrations of the gases dissolved in the liquid phase, since the values concerned are too small when calculated in weight units to be classed as important constituents of the solution phase, they produce only insignificant effects upon the solubility of the solids concerned. Probably a much greater variation can be attributed to variations in the composition of the solids, due to solid solution formation and to occlusion. The partial pressure of the carbon dioxide normally present in the atmosphere is too small to affect, to a recognizable degree, the concentration of the acid carbonate, which results from hydrolysis of the soluble carbonates. Hence, the nature of the entire system is established with a high degree of accuracy by the composition of the liquid phase.

# Composition of the Liquid Phase

No essential departures were made from the procedure outlined in the former papers of this series in determining the composition of solutions

Table I

Сом	position in Moles per 1000 Moles of V	Water of S	OLUTIONS S	SATURATED	AT 25°
	Saturated with	Na ₂ CO ₃	K2CO3	Na ₂ Cl ₂	K2Cl2
A	Na ₂ CO ₃ .10H ₂ O	50.63			
В	NaCl			54.90	10.5%
C	KCI			***	44.62
D	$K_2CO_3.^3/_2H_2O$		147.93		
E	K ₂ CO ₃ .3/ ₂ H ₂ O; NaKCO ₃ .6H ₂ O	18.50	135.70		
F	Na ₂ CO ₃ .7H ₂ O; NaKCO ₃ .6H ₂ O	60.40	39.70		
G	Na ₂ CO ₃ .10H ₂ O; Na ₂ CO ₃ .7H ₂ O	60.50	24.70		,
H	Na ₂ CO ₃ .10H ₂ O; NaCl	44.10		36.20	
I	NaCl; KCl			46.04	19.66
J	K ₂ CO ₃ .3/ ₂ H ₂ O; KCl		144.16		2.50
P	Na ₂ CO ₃ .10H ₂ O; NaCl; KCl	46.61		24.33	16.64
Q	Na ₂ CO ₃ .10H ₂ O; Na ₂ CO ₃ .7H ₂ O; KCl	45.90	33.60	16.30	
R	Na ₂ CO ₃ .7H ₂ O; NaKCO ₃ .6H ₂ O; KCl	47.33	38.79	13.17	
S	NaKCO ₃ .6H ₂ O; K ₂ CO ₃ . ³ / ₂ H ₂ O; KCl	18.72	133.50		2.22
Y	NaKCO ₃ .6H ₂ O	47.25	47.25		
U	NaKCO _{3.6} H ₂ O; KCl	43.80	43.80		11.80
0	Na ₂ CO ₃ .10H ₂ O; KCl	65.63			26.64

in equilibrium with the various solid phases. The thermostat used was kept constant to 0.1°. All determinations of potassium were made by separating and weighing as the chloroplatinate. Changes in the solid phases present were followed by a study of the crystal form and optical properties.

The composition of the saturated solutions finally obtained were calculated in terms of the number of grams per 100 g. of water and of moles per 1000 moles of water of the salts necessary to express its composition. The results are given in Tables I and II.

TABLE II

Сомр	osition in Grams per 100 Grams of	WATER OF S	OLUTIONS	SATURATEI	at 25°
	Saturated with	Na ₂ CO ₃	K2CO2	Na ₂ Cl ₂	K2Cl2
A	Na ₂ CO ₃ .10H ₂ O	29.78			
В	NaCl			35.66	
C	KCI	• • •			36.97
D	$K_2CO_3.^3/_2H_2O$		113.57		
$\mathbf{E}$	K ₂ CO ₃ .3/ ₂ H ₂ O; NaKCO ₃ .6H ₂ O	10.89	104.18		
F	Na ₂ CO ₃ .7H ₂ O; NaKCO ₃ .6H ₂ O	35.57	30.48	•••	
G	Na ₂ CO ₃ .10H ₂ O; Na ₂ CO ₃ .7H ₂ O	35.63	18.96		
H	Na ₂ CO ₃ .10H ₂ O; NaCl	25.97		23.51	
Ι	NaCl; KCl			29.88	16.29
J	K ₂ CO ₃ . ³ / ₂ H ₂ O; KCl		110.68		2.07
P	Na ₂ CO ₃ .10H ₂ O; NaCl; KCl	27.45		15.81	13.78
Q	Na ₂ CO ₃ .10H ₂ O; Na ₂ CO ₃ .7H ₂ O; KCl	27.03	25.79	10.59	
R	Na ₂ CO ₃ .7H ₂ O; NaKCO ₃ .6H ₂ O; KCI	27.86	29.78	8.55	
S	NaKCO ₃ .6H ₂ O; K ₂ CO ₃ .3/ ₂ H ₂ O; KCl	11.02	102.50		1.82
Y	NaKCO ₃ .6H ₂ O	27.82	36.29		
U.	NaKCO3.6H2O; KCl	25.79	33.64		9.78
0	Na ₂ CO ₃ .10H ₂ O; KCl	38.65			22.08

#### Graphical Representation of the System

Since the system represents a reciprocal salt pair, it can be represented graphically by the method of Löwenhertz as modified by van't Hoff, in which the composition expressed in terms of moles of Na₂Cl₂, K₂CO₃, K₂Cl₂ and Na₂CO₃ is plotted on two lines intersecting at 90°. The resulting diagram based upon the data of Table I is shown in Fig. 1, in which the letters represent "significant points." The positions of these points were fixed by averaging two or more results.

A large number of determinations, which are shown on the diagram as crosses, of points on the lines connecting significant points were found to be necessary to locate the course of these lines accurately. The departures from linear relations are in some cases surprisingly large.

As the hydrates here concerned readily form greatly supersaturated solutions and as long continued stirring was necessary to destroy this condition of supersaturation, great difficulty was found in correctly locating the limits of the fields on the left side of the diagram. The general course

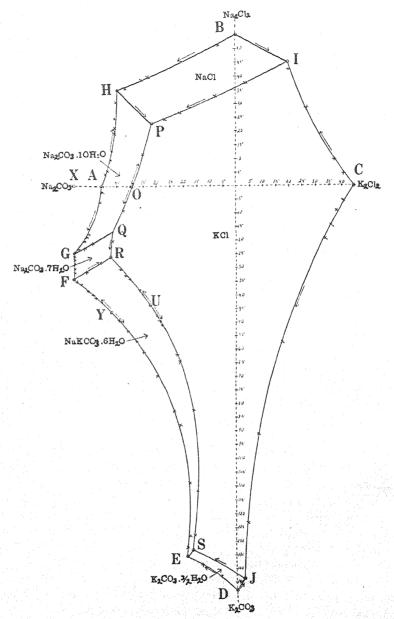


Fig. 1.—Equilibria between water and the carbonates and chlorides of sodium and potassium at  $25^{\circ}$ 

of the broken line A-G-F-E shows a satisfactory degree of agreement with a similar line determined by Kremann and Zitek¹⁰ at a temperature of ¹⁰ Kremann and Zitek, *Ber. Vinnee Akad.*, **11B**, 118 (1909).

24.2° as part of their work on the system, sodium carbonate-potassium nitrate. Since the solubility of the double salt is very greatly affected and that of the two hydrates of sodium carbonate is affected to a large extent by temperature changes, only rough agreement with their work in the location of the points G and F could be expected.

Although the five-halves hydrate frequently separated in solutions whose composition was represented by points along and beyond the limits of the line EF, no indications of a further break between A and E could be found in spite of the large number of determinations made. This salt also appeared in solutions corresponding to points in portions of the decahydrate, the heptahydrate, the double salt and the potassium chloride fields, but no definite limits within which it separated could be established, and the conclusion was reached that it was always metastable at this temperature.

The lines representing the changes in the composition of solutions which would result from evaporation at 25°, that is, the crystallization paths, have not been shown on the diagram, but their location can be indicated at least approximately with but little difficulty. For the fields representing solutions saturated with respect to Na₂CO₃.10H₂O, NaCl, KCl and K₂CO₃.3/₂H₂O, these lines must radiate from the points A, B, C and D respectively: for the heptahydrate field they must radiate from the point X, at the intersection of the lines CA and the prolongation of FG; for the double salt field they must radiate from Y, at the intersection of EF and the line bisecting the angle between AC and BD.

Each of the points A, B, C, D and Y represents a solution congruently saturated with respect to a single salt, and each of the points H, I, I, E and F a solution congruently saturated with respect to a pair of salts, but G is not congruently saturated. The points P, R and S represent solutions congruently saturated with respect to three salts, but Q is not a congruent solution although saturated with respect to three salts. Another congruent solution which is saturated with respect to the double salt and potassium chloride must be located on the line RS not far from Y. Its location can be fixed by the following procedure. From a study of the figures representing the composition of solutions on RS in the neighborhood of Y it can be estimated that the point in question should contain K2Cl2 to the extent of 11.8 moles. Starting at a point 11.8 units directly to the right of Y, and moving in a direction parallel to the diagonal bisecting the angle between AC and BD, the point at which RS is intersected, that is, the point U, will represent the one desired. Its composition, namely, 11.8 K₂Cl₂, 43.8 K₂CO₃, and 43.8 Na₂CO₃, is such that when evaporated it can lose double salt and potassium chloride in such proportions as to cause no change in its composition.

Still another congruent solution, which is saturated with respect to

Na₂CO₃.10H₂O and KCl, must be represented by a point on the line PQ. Since this solution must contain Na, CO₃, K and Cl in the same proportions as a solution prepared by dissolving sodium carbonate and potassium chloride in water, it must lie on the line AC. The point O therefore possesses the desired properties.

After having ascertained the locations of all the possible congruent solutions it can be predicted that all solutions represented by points lying above AC, except those on the periphery, will when evaporated ultimately attain the composition represented by P: solutions represented by points below YUC will reach S and those between these lines will reach R.

In conclusion it might be noted that this diagram illustrates the behavior of two kinds of congruent solutions. Those represented by H, I, J, E, F, P, R and S indicate the limiting values which can be attained in the composition of certain solutions when they are evaporated. They are crystallization end-points. Those represented by A, B, C, D, Y, U and O indicate points at which the character of the change in the composition of the solution resulting from evaporation changes abruptly. They are points from which certain crystallization paths take their origin.

# The System, Water and the Carbonates and Sulfates of Sodium and Potassium at 25°

The solid phases found to be concerned in the system, water and the carbonates and sulfates of sodium and potassium are, in addition to the carbonates described in discussing the chloride-carbonate system, potassium sulfate, the decahydrate of sodium sulfate and glaserite, a salt usually represented by the formula,  $3K_2SO_4$ . Na₂SO₄, but known to vary slightly as to the relative amounts of the two sulfates owing to the formation of a solid solution. The absence of anhydrous sodium sulfate from the entire system is worthy of comment. Possibly its absence is due to the formation of the sulfate carbonate of sodium to which the name "burkeite" has been given, which was found to separate at slightly higher temperatures. This salt may exist potentially in the form of complex ions at 25°, thereby reducing the concentration of the simple sodium ions and increasing the vapor pressure of the solution to such an extent as to prevent saturation with respect to the anhydrous salt. As in the former system, the fivehalves hydrate of sodium carbonate appears as a metastable phase only.

The composition of solutions saturated with respect to one or more of these solids is given in Tables III and IV, and a diagram based upon the data of Table III is given in Fig. 2. Very great difficulty was found in locating the line separating the potassium sulfate and glaserite fields, owing to the extreme slowness with which equilibrium was established in solutions whose composition corresponded to points near this line.

¹¹ Teeple, J. Ind. Eng. Chem., 13, 251 (1921).

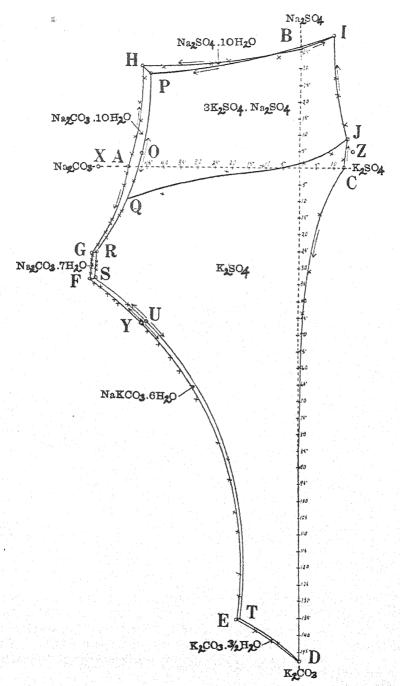


Fig. 2.—Equilibria between water and the carbonates and sulfates of sodium and notassium at 25°

TABLE III

	I ABLE II				
Сомя	POSITION IN MOLES PER 1000 MOLES OF W	ATER OF S	SOLUTIONS	Saturatei	) at 25°
	Saturated with	$Na_2CO_3$	$K_2CO_3$	Na ₂ SO ₄	$K_2SO_4$
A	Na ₂ CO ₃ .10H ₂ O	50.63			
В	Na ₂ SO ₄ .10H ₂ O			35.41	
C	K ₂ SO ₄				12.46
D	K ₂ CO ₂ .3/ ₂ H ₂ O		147.93		
E	K ₂ CO ₃ , 3/ ₂ H ₂ O; NaKCO ₃ , 6H ₂ O	18.50	135.70		
F	NaKCO ₃ .6H ₂ O; Na ₂ CO ₃ .7H ₂ O	60.4	39.70		
G	Na ₂ CO ₃ .10H ₂ O; Na ₂ CO ₃ .7H ₂ O	60.50	24.70		
H	Na ₂ CO ₃ .10H ₂ O; Na ₂ SO ₄ .10H ₂ O	46.60		30.50	
I	Na ₂ SO ₄ .10H ₂ O; K ₃ Na(SO ₄ ) ₂			39.27	9.36
J	K ₂ SO ₄ ; K ₃ Na(SO ₄ ) ₂			8.70	13.72
P	Na ₂ CO ₃ .10H ₂ O; Na ₂ SO ₄ .10H ₂ O;				
	K ₃ Na(SO ₄ ) ₂	44.30	3.69	32.28	
Q	Na ₂ CO ₃ .10H ₂ O; K ₂ SO ₄ ; K ₃ Na(SO ₄ ) ₂	57.30	9.60		6.50
R	Na ₂ CO ₃ .10H ₂ O; Na ₂ CO ₃ .7H ₂ O; K ₂ SO ₄	60.50	24.10		1.50
S	Na ₂ CO ₃ .7H ₂ O; NaKCO ₃ .6H ₂ O; K ₂ SO ₄	60.04	35.26	1.28	
T	NaKCO ₃ .6H ₂ O; K ₂ CO ₃ .3/ ₂ H ₂ O; K ₂ SO ₄	18.40	135.10		1.40
Y	NaKCO ₃ .6H ₂ O	47.25	47.25		
U	NaKCO ₃ .6H ₂ O; K ₂ SO ₄	46.50	46.50		1.30
0	Na ₂ CO ₃ .10H ₂ O; K ₃ Na(SO ₄ ) ₂	59.50		4.20	12.60
	Table I				
COMP	osition in Grams per 100 Grams of W		Solutions	Saturatei	AT 25°
	Saturated with	$Na_2CO_3$	K ₂ CO ₃	$Na_2SO_4$	K ₂ SO ₄
A	Na ₂ CO ₃ .10H ₂ O	29.78	••••	•••	
$\mathbf{B}$	$Na_2SO_4.10H_2O$		••••	27.94	
C	$K_2SO_4$		• • • •		12.08
D	$K_2CO_3.^3/_2H_2O$		113.57	• • •	
E	K ₂ CO ₃ .3/ ₂ H ₂ O; NaKCO ₃ .6H ₂ O	10.89	104.18		
F	NaKCO ₂ .6H ₂ O; Na ₂ CO ₃ .7H ₂ O	35.57	30.48		
G	NaCO ₃ .10H ₂ O; Na ₂ CO ₃ .7H ₂ O	35.63	18.96		
H	Na ₂ CO ₃ .10H ₂ O; Na ₂ SO ₄ .10H ₂ O	27.44	• • • • ,	24.06	
1	Na ₂ SO ₄ .10H ₂ O; K ₃ Na(SO ₄ ) ₂			30.98	9.34
J	$K_2SO_4$ ; $K_3Na(SO_4)_2$		• • • •	6.86	13.31
P	Na ₂ CO ₃ .10H ₂ O; Na ₂ SO ₄ .10H ₂ O;				
	$K_3Na(SO_4)_2$	26.09	3.58	25.46	
Q	$Na_2CO_3.10H_2O; K_2SO_4; K_3Na(SO_4)_2$	33.74	7.37	• • •	6.30
R	Na ₂ CO ₃ .10H ₂ O; Na ₂ CO ₃ .7H ₂ O; K ₂ SO ₄	35.63	18.50		1.45
S	Na ₂ CO ₃ .7H ₂ O; NaKCO ₃ .6H ₂ O; K ₂ SO ₄	35.35	27.07	1.01	• • •
T	NaKCO ₃ .6H ₂ O; K ₂ CO ₃ .3/ ₂ H ₂ O; K ₂ SO ₄	10.83	103.72	•••	1.36
Y	NaKCO ₃ .6H ₂ O	27.82	36.29	• • •	
U	NaKCO ₃ .6H ₂ O; K ₂ SO ₄	27.38	35.71		0.97
0	Na ₂ CO ₃ .10H ₂ O; K ₃ Na(SO ₄ ) ₂	41.65		3.31	9.40

The crystallization paths for fields representing solutions saturated with respect to Na₂CO₃.10H₂O, Na₂SO₄.10H₂O, K₂SO₄, and K₂CO₃.³/₂H₂O must radiate from the points A, B, C and D. The form of the field for the solid Na₂SO₄.10H₂O is difficult to visualize without a space model of which Fig. 2 is only a projection. The paths for the heptahydrate of sodium

carbonate and the double carbonate fields must radiate from the points X and Y, whose positions are located by the construction indicated in the preceding system. Assuming that glaserite has a constant composition indicated by the formula given, the crystallization paths for the glaserite field must radiate from the point Z, obtained by prolonging IJ until it intersects a line representing solutions containing three times as many moles of potassium as of sodium sulfate. Owing to variations in the composition of this solid the directions of these paths can only be indicated with approximate accuracy.

The points A, B, C, D and Y must represent solutions congruently saturated with respect to a single salt and the points H, I and E with respect to two salts, but G and J are not congruently saturated. There must also be a point on the line connecting C and D representing a solution congruently saturated with respect to potassium sulfate and the three-halves hydrate of potassium carbonate, but its position is so near to D that it cannot be indicated properly on the diagram. Expressed otherwise the solubility of potassium sulfate in solutions saturated with potassium carbonate is negligible.

From a study of the directions of the crystallization paths it becomes obvious that the points P, S and T represent solutions congruently saturated with respect to three salts, but Q and R are not congruently saturated.

Another congruent solution, which is saturated with respect to potassium sulfate and the double carbonate, must be located on the line ST not far from Y. Its position can be fixed by the following procedure. Solution S contains 1.28 moles of potassium sulfate and T 1.4 moles; therefore a point on the line ST not far from Y might be expected to contain 1.3 moles. Starting from a point located 1.3 units to the right of Y and moving along a line parallel to the line bisecting the angle between AC and BD, the line ST will be intersected at U, which will represent the desired point. It contains in addition to 1.3 moles of  $K_2SO_4$ , 46.5 of  $K_2CO_3$  and 46.5 of  $Na_2CO_3$ .

Still another congruent solution must be located on the PQ line. Its composition can be established roughly by a series of approximations to be 59.5 Na₂CO₃, 4.2 Na₂SO₄, and 12.6 K₂SO₄. The point in question must be located not far from A but slightly above AC. The number of moles of sodium carbonate present can be estimated to be 59.5, basing the estimate upon the rate at which sodium carbonate changes between P and Q. Starting on AC at a point 59.5 units to the right of the origin and proceeding therefrom in a line parallel to the line which represents three times as many moles of potassium as of sodium sulfate it will be found that PQ is intersected at O. This point corresponds to the composition indicated above, and contains that number of moles of sodium carbonate and a total number of moles which its position with respect to

P and Q requires. This procedure involves rather large errors and assumes that the rate at which the composition of the solution changes along the line PQ is uniform as to sodium carbonate and the total number of moles present.

Having fixed the position of O it can be predicted that all solutions represented by points above AOZ except those on the periphery must finally attain the composition P when evaporated. Further owing to the fact that certain crystallization paths pass into the glaserite field from the potassium sulfate field there will be a small triangular area limited by the point C, the intersection of OZ and QJ and the line OZ representing solutions which have the same crystallization end-point. In a like manner it can be predicted that that portion of the diagram limited by the two areas already defined and the line YUC represents solutions for which the crystallization end-point is S, and those portions below the last named line represent solutions for which T is the crystallization end-point.

#### Summary

- 1. Certain optical and crystallographic properties of the hydrates of sodium carbonate and of the hydrate of the double sodium-potassium carbonate have been ascertained, which can be used in identifying these compounds by means of the microscope.
- 2. The solubility data necessary for the preparation of complete phase-rule diagrams for the systems H₂O-Na₂CO₃-KCl and H₂O-Na₂CO₃-K₂SO₄ at 25° have been determined.

BERKELEY, CALIFORNIA

[Contribution from the Chemical Laboratory of Clark University, No. I, 37]

# STUDIES RELATING TO METALLO-ORGANIC COMPOUNDS. IV. THE CONDUCTANCE OF TRIMETHYL STANNYL CHLORIDE IN MIXED SOLVENTS

By Charles A. Kraus and Willard N. Greer Received October 6, 1923

In preceding numbers of this series it has been shown that the alkyl tin halides are non-conductors when dissolved in solvents of the non-basic type and conductors in solvents of the basic type, I such as the amines and the alcohols. It has further been shown that the alkyl metal halides exhibit a marked tendency to combine with ammonia and the amines to form compounds having markedly higher melting points than either of the constituents. While in some instances two molecules of ammonia or amine may combine with an alkyl metal halide, in by far the greater number of instances only a single molecule is involved. Where two molecules of am-

Kraus and Callis, This Journal, 45, 2624 (1923).

² Kraus and Greer, ibid., 45, 3078 (1923).

monia or amine combine with an alkyl metal halide, one molecule is, as a rule, held rather loosely while the other is held much more firmly. This is well illustrated by the compounds of ammonia with trimethyl tin iodide, in which case one molecule of ammonia is lost readily at ordinary temperatures, while the second molecule cannot be removed by ordinary means, the compound subliming at higher temperatures or in a vacuum at lower temperatures.

It has been suggested that the electrolytic properties of the alkyl metal halides and of other similar compounds are due to the formation of a complex cation of the ammonium type; for instance, trimethyl tin chloride and ammonia combine to form the compound H₃NSn(CH₃)₃Cl, in which the trimethyl tin group is attached to pentavalent nitrogen.¹ This accounts for the absence of electrolytic properties in the case of the pure compounds, as well as in that of solutions of these compounds in non-basic solvents of higher dielectric constant. This view as to the constitution of these compounds may be checked up by studying the conductance of the alkyl metal halides in solution in non-basic solvents on the addition of varying quantities of a basic solvent such as an amine or an alcohol. In the present article data relative to a number of systems of this type are given.

#### Experimental Part

Measurements were carried out in the usual way, according to the Kohlrausch method, with such improvements as are commonly practiced at the present time. The cell employed for the measurements was that previously employed and described by Kraus and Kurtz.³ All measurements were carried out at  $25.00^{\circ} \pm 0.01$ .

Conductance of Trimethyl Tin Chloride in Nitrobenzene on Addition of Pyridine.—A 0.1 N solution of trimethyl tin chloride in nitrobenzene was prepared in the cell, by weighing 9.2234 g. of trimethyl tin chloride into

Table I

Conductance of 0.1 N Solution of (CH₃)₈SnCl in Nitrobenzene in the Presence of Various Amounts of Pyridine at 25°

Moles pyridine per liter	Spec. cond. × 104	Moles pyridine per liter	Spec. cond. × 104
0.00676	0.125	0.29	0.324
.0149	.149	0.37	.334
.0249	.167	0.44	.345
.033	.179	0.513	.351
.0416	.190	0.59	.356
.0503	.199	0.66	.359
.059	.208	0.76	.363
.0835	.228	0.84	.364
.119	.254	0.93	.367
.209	.295	1.05	.368

³ Kraus and Kurtz, This Journal, 44, 2463 (1922).

462.96 cc. of nitrobenzene. Pyridine was added to the nitrobenzene solution by means of a weight pipet of the type described by Kraus and Callis.¹ The cell was placed in the thermostat, pyridine was added in various amounts and the conductance of the solution measured. The results are given in Table I, which requires no further explanation.

The results are shown graphically as Curve I, Fig. 1.

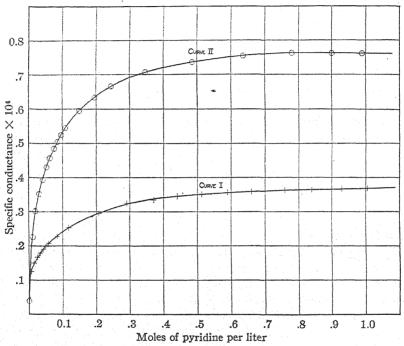


Fig. 1.—The increased conductance of solutions of trimethyl tin chloride in nitrobenzene (Curve I) and acetone (Curve II) on addition of pyridine

Conductance of Trimethyl Tin Chloride in Acetone in the Presence of Pyridine.—A 0.1 N solution of trimethyl tin chloride in acetone was prepared in the cell, with 7.7161 g. of trimethyl tin chloride in 387.32 cc. of acetone. The specific conductance of the acetone was  $7.4 \times 10^{-7}$ . Pyridine was added as before by means of a weight buret. The results are given in Table II.

The results are shown graphically as Curve II, Fig. 1.

Conductance of Trimethyl Tin Chloride in Mixtures of Acetone and Alcohol.—To a solution of 250 cc. of 0.1 N solution of trimethyl tin chloride in acetone prepared in the cell was added successively 25 cc. of 0.1 N solution of trimethyl tin chloride in alcohol, the conductance of the mixture on successive additions being measured. The same procedure

Table II

Conductance of 0.1 N Solutions of  $(CH_3)_5SnCl$  in Acetone in the Presence of Various Amounts of Pyridine

Moles pyridine per liter	Spec. cond. × 104	Moles pyridine per liter	Spec. cond. × 104
0.0	0.0389	0.109	0.544
.0121	.225	.150	.594
.0198	.302	.195	.633
.0309	.352	.244	.666
.0419	.393	.345	.707
.0536	.430	.485	.738
.0635	.457	.636	.755
.0747	.484	.78	.763
.085	.504	.90	.763
.096	.524	.99	.763

was then repeated, in which 25 cc. of  $0.1\,N$  solution of trimethyl tin chloride in acetone was successively added to 250 cc. of  $0.1\,N$  solution of trimethyl tin chloride in 95% alcohol. The results are given in Table III.

Table III  $\begin{tabular}{ll} \textbf{Conductance of } 0.1 N \textbf{Solutions of } (\textbf{CH}_3)_8 \textbf{SnC1} \textbf{ in Mixtures of Acetone and } 95\% \\ \textbf{Alcohol.} \\ \end{tabular}$ 

Volume per cen alcohol	t, Spec. cond.	Volume per cent. alcohol	Spec. cond. × 104
0	0.059	55	1.357
5	0.185	60	1.494
1.0	0.295	65	1.654
15	0.416	70	1.849
20	0.542	75	2.087
25	0.670	80	2.375
30	0.794	85	2.737
35	0.917	90	3.176
40	1.034	95	3.753
45	1.149	100	4.348
50	1.242		

The results are shown graphically as Curve III, Fig. 2.

Conductance of Trimethyl Tin Chloride in Mixtures of Nitrobenzene and Pyridine.—Mixtures of pyridine and nitrobenzene were prepared as in the case of acetone and alcohol and the conductance of these mixtures measured. The pyridine was purified by treating 600 cc. of a sample which boiled at 116–118° with solid sodium hydroxide. The mixture was refluxed for 5 hours, the pyridine decanted and distilled. After three successive distillations a product was obtained which boiled at 115° and gave the value  $0.12 \times 10^{-6}$  for the specific conductance. The nitrobenzene was purified by redistilling a commercial product several times. A constant-boiling sample was obtained which gave a value of  $0.31 \times 10^{-6}$  for the specific conductance. The results are given in Table IV.

 $\label{total conductance} Table~IV$  Conductance of 0.1 N Solutions of (CH3)3SnCl in Mixtures of Nitrobenzene and Pyridine

Volume per cent. alcohol	Spec. cond. × 104	Volume per cent. alcohol	Spec. cond. X 104
0	0.0019	55	0.421
5	.338	60	.420
10	.383	65	.418
15	.403	70	.412
20	.415	75	.396
25	.423	80	.387
30	.427	85	.373
35	.429	90	.354
40	.430	95	.328
45	.430	100	.295
50	.429		

The results are shown as Curve IV, Fig. 2.

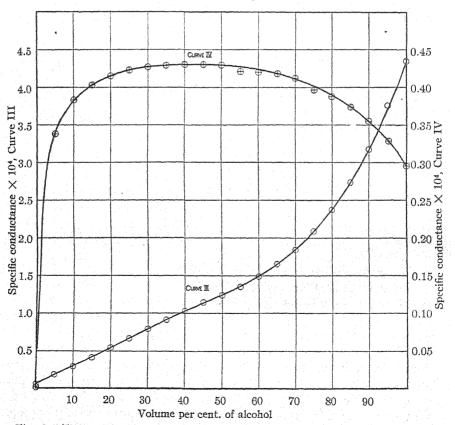


Fig. 2.—The conductance of solutions of trimethyl tin chloride in mixtures of acetone and alcohol (Curve III) and nitrobenzene and pyridine (Curve IV)

#### Discussion

In the tables the values of the specific conductance times 10⁴ are given. If in Tables I and II the change in volume due to the added pyridine is neglected, then the equivalent conductance will have the same numerical values as given in the column of specific conductances. If the volume change on mixing solutions of pyridine and alcohol and pyridine and nitrobenzene be neglected, then the values of the equivalent conductance are equal to the numerical values given under the columns headed specific conductance.

An examination of the tables and of the figures shows that the properties of solutions of trimethyl tin chloride in acetone and nitrobenzene are chiefly determined by the amount of pyridine which has been added. Considering the results of Tables I and II, shown in Fig. 1, it is seen that the addition of even a small amount of pyridine causes a very large rise in the conductance of the solution. Thus the addition of approximately 0.01 moles of pyridine to 0.1 moles of trimethyl tin chloride in acetone raises the conductance from 0.0389 to 0.225. With further addition of pyridine, further increase of the conductance takes place, so that on the addition of approximately one mole of pyridine the conductance reaches a value of 0.763. As may be seen from the curve, every successive addition of pyridine causes a smaller and smaller rise in the value of the conductance. What holds true of solutions in acetone on addition of pyridine equally holds true for solutions in nitrobenzene on addition of the same compound. This form of the curve is in harmony with the view that the electrolytic properties of these solutions are due to the formation of a salt-like compound between trimethyl tin chloride and pyridine. The values of the ionization in the different solvents can be compared only roughly. The specific conductance of a 0.1 N solution of trimethyl tin chloride in nitrobenzene containing approximately one mole of pyridine is 0.368, while for a corresponding solution in acetone it is 0.763. The fluidity of nitrobenzene at 25° is approximately 54.3, while that of acetone is 304 at 18°. In other words, the fluidity of acetone is about 6 times that of nitrobenzene. In proportion to the fluidity of the solvent medium, therefore, solutions of trimethyl tin chloride in the presence of pyridine are relatively better conductors in nitrobenzene than in acetone, corresponding to the relatively greater dielectric constant of nitrobenzene.

Considering Fig. 2, Curve IV, it is seen that the conductance of  $0.1\,N$  solutions of trimethyl tin chloride in mixtures of nitrobenzene and pyridine exhibits a maximum in the neighborhood of 42 volume per cent. of pyridine. The fluidity of pyridine is markedly higher than that of nitrobenzene. It follows, therefore, that the ionization of trimethyl tin chloride in the mixtures lies still nearer the axis of nitrobenzene.

The initial additions of pyridine to nitrobenzene cause a very marked

increase in the conductance due to the formation of the complex ammonium salt,  $C_6H_5NSn(CH_3)_3Ci$ . The addition of nitrobenzene to the pyridine solution causes an increased conductance as a result of increased ionization due to the greater dielectric constant of nitrobenzene.

The form of the curve for mixtures of acetone and alcohol, as shown in Fig. 2, differs markedly from that for mixtures of nitrobenzene and pyridine. The initial additions of alcohol to acetone cause a marked increase of conductance very nearly as a linear function of the volume composition of the solution. In view of the fact that the fluidity of acetone is much higher than that of alcohol, this indicates a marked increase in the ionization of the electrolyte. The effect, however, is much less marked than it is in the case of mixtures of pyridine and nitrobenzene or pyridine and acetone. Probably acetone itself forms a complex oxonium compound in solution to some extent: and, while alcohol, without doubt, forms a complex oxonium compound with trimethyl tin chloride, it is, in all likelihood, much less stable than the corresponding pyridine compound, which is in agreement with the fact that trimethyl tin chloride is obtained in the pure state on evaporation of the alcohol, whereas in the case of pyridine a compound remains behind. The initial additions of acetone to the alcohol solution cause a marked decrease in the conductance due, without doubt, to a markedly decreased ionization. This is probably in part due to a decrease in the dielectric constant, but probably even on addition of small amounts of acetone the equilibrium of the complex may be measurably affected. In this connection it should be noted that the conductances of solutions containing larger amounts of alcohol are, without doubt, measurably affected by the presence of water. The conductance of a 95% alcohol solution, without addition of acetone, is much higher than would correspond to the conductance of a solution in absolute alcohol, according to measurements recorded by Kraus and Callis,1 thus indicating a marked influence of water on the conductance of trimethyl tin chloride in al-

Similar changes in the conductance of solutions on addition of suitable substances have previously been recorded in a few instances. In the first place, solutions of salts, which show a marked tendency to take up water of crystallization, exhibit a low degree of ionization in non-aqueous solvents and their ionization is greatly increased on addition of water or an alcohol. This is particularly noticeable in the case of calcium nitrate on addition of water and the alcohols to solutions in acetone. Lithium salts exhibit a similar, although less marked, behavior.

These cases, however, are not strictly analogous to those which form the subject of the present investigation. The behavior of the acids in various non-aqueous solvents on addition of water forms perhaps a much closer

⁴ Jones, Bingham and McMaster, Z. physik. Chem., 57, 193, 257 (1906).

analogy with that of the alkyl metal halides. It has been shown that the ionization of the acids in the alcohols is greatly increased on addition of water. This effect has been ascribed to the formation of a compound of the oxonium type, which is more highly ionized than the pure acid⁵ or, perhaps better, the alcoholated acid.

Trimethyl tin chloride, as has previously been pointed out, exhibits properties which resemble those of the halogen acids very closely. They are non-conductors in the pure liquid condition, 6 as well as in solvents of the non-basic type, they are conductors in solvents of the basic type, or in solvents of the non-basic type to which small quantities of solvents of the basic type have been added, they are relatively weakly ionized in solvents of the mean dielectric constant, and they conform to the law of mass action in solvents of relatively high dielectric constant. What is true of trimethyl tin chloride is, without doubt, also true of other metallo-organic compounds of the type  $M^nR_{n-1}X$ . The properties of these compounds may be accounted for on the assumption that the group (CH₃)₃Sn occupies an intermediate position in the potential series, which brings it into the same class with hydrogen. Indeed, the group in its compounds resembles hydrogen much more closely than do the elements which occupy a corresponding position in the potential series, owing to the fact that the groups are univalent, while the corresponding elements have a relatively high valence. However, as was pointed out by one of the present authors, these elements likewise exhibit the property of acting amphoterically, that is, either positively or negatively, which is also a property of hydrogen and of groups of the type of the trimethyl tin group and other similar groups, as will be shown in a subsequent article.

⁵ Goldschmidt, Z. physik. Chem., 89, 132 (1915). Kailan, ibid., 89, 678 (1915). Braune, ibid., 85, 170 (1913).

⁶ Substances which are not marked conductors of the electric current in the pure liquid condition are not to be classed as true electrolytes, even though solutions of such substances in certain solvents may exhibit electrolytic properties. Present evidence indicates that the electrolytic properties of such substances in solution are due to the formation of new compounds which are true electrolytes. No term has thus far been suggested to distinguish substances of this type from true electrolytes; that is, substances which are ionized in the liquid condition as well as in solution. It is suggested that the term pseudo-electrolyte might be employed to distinguish the class of substances here under discussion from the true electrolytes. This prefix is now commonly used to distinguish between the true acids and certain organic substances which exhibit acidic properties in solution due to a rearrangement. The extension of the use of this prefix to compounds other than the acids should lead to no confusion, while at the same time it would serve to characterize a class of substances which is widely represented. A pseudo-electrolyte would thus be a compound which itself does not exhibit electrolytic properties but which reacts with certain solvents to form a new compound which is a true electrolyte.

⁷ Kraus, Rec. trav. chim., 42, 588 (1923).

#### Summary

The conductance of solutions of trimethyl tin chloride in nitrobenzene and acetone on addition of small amounts of pyridine has been measured. A marked increase takes place in conductance on addition of pyridine, and this effect is the greater, the smaller the amount of pyridine already present.

The conductance of solutions of trimethyl tin chloride in mixtures of 0–100% of acetone and alcohol and nitrobenzene and pyridine has been measured. The initial conductance in nitrobenzene is extremely low, indicating that trimethyl tin chloride is practically un-ionized in this solvent. The initial conductance in acetone is markedly higher than in nitrobenzene. While the conductance in acetone on addition of alcohol is increased, this increase is much less marked than it is on addition of pyridine.

The results are in agreement with the view that trimethyl tin chloride itself is not a true electrolyte and that its electrolytic properties in solution are due to the formation of compounds of the oxonium and ammonium type, the trimethyl tin group transferring from chlorine to tetravalent oxygen or pentavalent nitrogen, respectively.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

#### THE ATOMIC WEIGHT OF LEAD FROM THE BELGIAN CONGO

By Theodore W. Richards and Paul Putzeys¹
Received October 11, 1923

The fundamental relation of the isotopes of lead to the process of radioactive disintegration gives an especial interest to the atomic weights of these isotopes. The difference in the geological histories of uranium deposits in different parts of the world makes it especially desirable that the quantitative relations of the lead in deposits from as many widely separated localities as possible should be examined. Within the past few years, as is well known, a new source of uranium and radium material has been found in the Belgian Congo. Accordingly, we have investigated the atomic weight of lead derived from this source.

The metal employed was obtained from a mixture of several minerals existing in the center of Africa. These all doubtless originated in a common primary deposit of uraninite, of which an analysis has been published.^{2a} Among the decomposition products of this primary mineral, Schoep^{2b} has discovered several secondary minerals containing lead, namely, curite (2PbO.5UO₃.4H₂O), kasolite (3PbO.3UO₃.3SiO₂.4H₂O), dewindtite (4PbO.-8UO₃.3P₂O₅.12H₂O) and stasite (4PbO.8UO₃.3P₂O₅.12H₂O). In all these

¹ Fellow for the Commission for Relief in Belgium Educational Foundation.

^{2a} Steinkuhler, Bull. soc. chim. Belg., 32, 233 (1923).

^{2b} Schoep, Compt. rend., 173, 1186, 1476 (1921); 174, 623, 875 (1922).

minerals, the lead was probably chiefly derived from the uraninite—the end-product of a large amount of uranium which had undergone disintegration. The specimen upon which we worked was from a mixture of all these minerals, and was obtained through the kindness of Professor W. Mund, of Louvain, Belgium. Monsieur Clérin, chief chemist of the Hoboken plant of the Compagnie minière du Katanga, has since been so kind as to give us larger amounts of the same material; to both we express our hearty thanks. This lead apparently may be available in quantity, and may therefore be used for a great variety of large scale experiments on the comparison of isotopes. For this reason, especially, a determination of its atomic weight is of value. A qualitative test by means of the gold-leaf electroscope showed appreciable radioactivity.

The method of determination adopted in the present research was essentially the same as that used by Baxter and his assistants³ in the study of the atomic weight of ordinary lead, and by others in this Laboratory for the determination of the atomic weight of uranium lead.⁴ For this reason a very brief account suffices.

#### Purification of Materials

The methods employed for the purification of nitric acid, water and the several gases used in the work needed no variations from the usual procedure. The silver we owe to the kindness of Dr. Norris F. Hall, who prepared a large quantity of the metal in a very pure state for coulometric work several years ago.⁵

The preparation of the lead deserves more detailed treatment. For comparison with the radioactive sample and for practice, a small sample of ordinary lead chloride was prepared from c. p. lead nitrate (once recrystallized) by precipitation in dilute solution by hydrochloric acid. The chloride was recrystallized twice from slightly acidified water. Although not very thoroughly purified, it was pure enough to serve as a basis for practice analyses and to show that the details of the analytical process were well in hand. This was designated as Specimen A.

The radioactive metal (which had been already purified considerably by commercial methods) was dissolved in pure nitric acid, the solution filtered and evaporated, and the lead nitrate recrystallized thrice, the last of these recrystallizations being conducted in quartz dishes. The solution of the purest nitrate was filtered again through a Gooch-Monroe platinum crucible, and subsequently lead chloride was precipitated from it by pure hydrogen chloride. After two recrystallizations (using purest water and quartz dishes) the recrystallized lead chloride was carefully dried for anal-

- ³ Baxter and others, This Journal, 30, 187 (1908); 37, 1020, 1027 (1915).
- ⁴ Richards and others, *ibid.*, **36**, 1329 (1914); **38**, 2613 (1916); **39**, 531 (1917). Smithsonian Report for 1918, p. 205, Pub. No. 2557.
  - ⁵ Richards and Hall, This Journal, 39, 531 (1917); 38, 2045 (1916).

ysis; it constituted Sample B. From the mother liquors of this preparation, the residual chloride was precipitated by concentration and by addition of hydrochloric acid, and was recrystallized. It was then converted into the nitrate by repeated evaporation with the purest nitric acid, and the nitrate was recrystallized thrice from very acid solutions. Two more recrystallizations as nitrate from the purest water and filtration through a Gooch-Monroe crucible provided a very pure solution of the nitrate, which was precipitated by a solution of the purest hydrochloric acid. Three recrystallizations of the lead chloride from the purest water acidified with a few drops of hydrochloric acid (with centrifugal draining, as usual) yielded a preparation C. This specimen was doubtless purer than Specimen B, having received much more careful treatment and many more recrystallizations. The several samples were kept dry in quartz dishes in desiccators containing solid caustic alkali.

#### Method of Analysis

Seven analyses were made of these several samples. The method may be very briefly outlined.

The lead chloride was fused in a platinum boat in a current of pure hydrogen chloride. This gas having been displaced by pure nitrogen during the cooling, the product was finally enclosed in a weighing bottle in a current of pure dry air by means of the well-known bottling apparatus usually employed in such work. In every case the fused lead chloride was entirely colorless and transparent; but upon dissolving it in warm water slightly acidified with nitric acid in a suitable Erlenmeyer flask, traces of insoluble black residue were found floating on the surface of the water, especially in Specimens A and B. This impurity was collected on a tared Gooch-Monroe crucible, and weighed, and the weight was duly subtracted from the weight of the chloride. The average weight

TABLE I DATA AND RESULTS

	- 4	WIY WAN TOPORTIO		
Analysis	Corrected wt. fused PbCl ₂ in vacuum	Corrected wt, equivalent Ag in vacuum	Ratio PbCl ₂ /Ag	Atomic weight
	Sa	mple A. Ordinar	y lead	
1	5.70194	4.42331	1.28906	207.21
2	4.65819	3.61405	1.28891	207.18
3	4.87664	3.78388	1.28879	207.15
				Av. 207.18
	Sample B.	Congo lead (prelin	ninary analyses	3)
4	3.38089	2.63325	1.28392	206.10
5	4.21302	3.28093	1.28409	206.14
				A 000 10
	Sample C	Congo lead (fir		Av. 206.12
6	3.66388	2.85263	1.28439	206.20
7	4.30262	3.34997	1.28438	206.20
				-
				Av. 206.20

The data are calculated for Ag = 107.88 and C1 = 35.458.

of the contamination, the nature of which was not determined, was (counting all determinations) less than 0.2 mg., and in the last two (the most important) determinations, less than 0.1 mg. The platinum boat was weighed before and after each analysis and its average loss of weight found to be only 0.07 mg.

The clear solution of the lead chloride used occupied a volume of about 1.5 liters; it was precipitated with a suitable weighed amount of purest silver which had been dissolved, with the usual precautions, and the end-point was adjusted with the help of a few cubic centimeters of very dilute standard solutions of silver nitrate and hydrochloric acid by means of a nephelometer.

The rough preliminary analyses of ordinary lead chloride (Nos. 1, 2 and 3) for which no great accuracy is claimed, nevertheless yielded results (in average 207.18) sufficiently concordant with themselves and with the accepted value of the atomic weight of lead, 207.20, for the present purpose. The two following analyses upon the Congo lead (Nos. 4 and 5) likewise suffered from minor defects and were made with material only roughly purified. On the other hand, the final analyses (Nos. 6 and 7) were made with material far more carefully purified, and every step of each analysis was satisfactory. The loss in weight of the platinum boat and the weights of black residue were so small as to be practically negligible, and the end-point test in the nephelometer was unusually satisfactory. Further analyses seemed to be unnecessary, since these left nothing to be desired.

Evidently, lead from the uranium deposits in the Congo has an atomic weight exactly one unit less than the atomic weight of ordinary lead, and perhaps only 0.14 unit higher than that of pure uranium lead. Apparently, then, we may infer (assuming that the material contains nothing but a mixture of uranium lead and ordinary lead) that about 88% of the material under investigation consisted of uranium lead, and only 12% of ordinary lead. This is a far lower percentage of ordinary lead than that existing in the similar metal from Australia. The result leaves little room for doubt that the lead which forms an integral part of the four new radioactive minerals was really derived chiefly from uranium lead. The uranium lead from the disintegration must afterwards have combined chemically with much of the residual undisintegrated uranium. Clearly, these minerals must have been formed long after the original deposit of uraninite crystallized in its bed. In this case, as in others, a careful study of the atomic weight of the mixed isotopes in relation to the coexistent minerals thus affords an interesting clue concerning the geological history of the region.

In conclusion we are glad to express our indebtedness to the Education Foundation of the Commission for Relief in Belgium and to the Carnegie Institution of Washington for pecuniary assistance.

#### Summary

The atomic weight of a sample of radioactive lead obtained from a mixture of minerals found in radium ore from the Belgian Congo was determined as 206.20, as compared with a control sample of ordinary lead which gave the value 207.18. Evidently, therefore, the lead in these minerals consisted chiefly of uranium lead; and the minerals must have been formed long after the original deposit of uraninite.

Cambridge 38, Massachusetts

#### NOTES

A New Light Filter.—As far back as 1904 I observed accidentally that a solution of ordinary chrome alum of a proper concentration and thickness of layer is admirably adapted for detecting the potassium flame when it is masked by the presence of an excess of sodium light. It was found later by Mr. William D. Pardoe, a graduate student working in my laboratory, that it was possible to prepare a light filter with a solution of chrome alum which absorbs *completely* not only sodium light but that of lithium, strontium, calcium and barium. Viewed through such a filter the potassium flame is seen to rise from the glowing platinum loop in the form of a long, crimson, very bright streamer when a relatively large amount of this element is present, and less so, but always perceptible, as the quantity diminishes. Under the circumstances the flames of rubidium and cesium are also visible, but since these elements occur only in a few localities and in the minutest amounts, they are not apt to mislead one.

The filter is as sensitive as it is reliable and will keep indefinitely. One which has been in use off and on for fifteen years is as efficient today as it was when first prepared. In some cases, it has proved even more reliable than a Browning direct vision spectroscope. Such a filter is very handy in testing for potassium in the residues obtained by the evaporation of mineral and other waters, and in examining mineral silicates and silicate rocks for this element. Insoluble siliceous materials should be finely powdered, mixed with (a) pure gypsum or (b) four parts of pure calcium carbonate and one part of resublimed ammonium chloride, and the mixture made into a thick paste with water. A bit of the paste is then collected in a loop on the end of a platinum wire, brought into the fusion zone of the Bunsen burner, and the flame viewed through the filter.

To prepare a number of these filters (they will be found very useful in the laboratory for qualitative analysis), dissolve 310 g. of crystallized chrome alum in a large flask in a liter of water by gentle heating, cool and filter the solution and fill with it glass bottles of square prismatic form. Those used by me are 10 cm. high from bottom to shoulder, and the lateral edge measures 4.7 cm. Ordinary wooden corks will serve as stoppers. The filter is best held upright, very close to the eye, and about 5 or 6 cm. from the flame of the burner.

A Possible Reconciliation of the Octet and Positive-Negative Theories of Chemical Combination.—I have recently had the opportunity of reading, in proof, the monograph by Professor G. N. Lewis on "Valence and the Structure of Atoms and Molecules" which has just appeared as a volume of our Scientific Series of Monographs. One of the most fundamental concepts of the theory proposed by Professor Lewis is that a pair of electrons forms the bond which holds two atoms in combination. In nearly all reactions, whether those of electrolytes in solutions or of organic or other compounds, two atoms of one compound separate and combine with two atoms of some other compound. The atoms of the second compound must also separate. Professor Lewis has not, I think, discussed what happens to the electrons in these processes of separation and recombination.

Two methods of separation between two atoms held together by a pair of electrons seem possible: one electron may remain with each atom, leaving both atoms electrically neutral; or the pair of electrons may remain with one of the atoms, which will in that case be negative, while the other atom will be positive. It will be admitted by everyone that electrolytes react in the second manner. There are many considerations which point to the conclusion that many other compounds react in a similar manner.

In the case of hydrogen, it is generally agreed that the hydrogen atoms of acids separate from oxygen, or some other element with which they are combined, without any electron. Since we have among the organic compounds all degrees of ionization from that of strong acids to that of substances like ethyl alcohol, which ionize even less than water, and since ionic hydrogen is very easily transferred from oxygen to carbon and vice versa, in tautomeric compounds, we seem to be justified in assuming that in nearly or quite all reactions hydrogen atoms separate from carbon in the positive form and the carbon atoms from which they separate must, therefore, be left in the negative form. In this sense that they either cling to or give up easily the pair of electrons which unites them to other atoms, carbon and other atoms in organic compounds are either positive or negative. This point of view is often useful in predicting the course of a reaction. For instance, in the addition of ammonia, hydroxylamine, phenylhydrazine or the Grignard reagent to aldehydes or ketones, the hydrogen or magnesium always adds itself to the oxygen atom, which clings obstinately to the pair of electrons. In the hydrolysis of cyanides, R-C=N, the nitrogen atom clings to the electrons and the hydrogen atoms attach themselves to that, while the negative hydroxyl adds itself to the carbon.

In the separation of two carbon atoms in breaking the double union of the type R—CH:: CH₂, the pair of electrons clings chiefly to the end

carbon atom, which becomes, in that way, negative and the hydrogen adds to that, while the bromine or iodine of hydrobromic or hydriodic acid adds to the second, positive carbon atom. In a similar manner, when nitrogen trichloride adds to the same compound, the positive chlorine adds to the end carbon atom while the negative nitrogen atom of the nitrogen dichloride group adds to the second carbon atom.¹

The theory here presented does not require us to assume that in a molecule of chlorine, Cl: Cl, one of the chlorine atoms is positive and the other negative. It does assume, however, that when the molecule separates into two atoms, in a reaction with some other compound, the pair of electrons usually remains with one of the atoms, which is therefore negative, while the atom which separates without the electrons is positive.

The theory does not require us to suppose, either, that an atom which enters a molecule in a positive form must necessarily leave the molecule in the same form. Thus, in the addition of hypochlorous acid to ethylene the positive chlorine atom is added to one of the carbon atoms and the negative hydroxyl to the other.² But the ethylene chlorohydrin, CH₂Cl—CH₂OH, formed hydrolyzes to glycol, CH₂OH—CH₂OH, and hydrochloric acid. The chlorine adds in the positive form and splits off in the negative. Such a result seems quite natural according to the theory as here presented, but it is rather difficult to account for by the positive-negative theory as it has often been interpreted.

The view here presented is closely related to a suggestion made in the author's address before the St. Louis Congress of Arts and Sciences, namely, that molecules separate into positive and negative ions as they react with each other.³

In the foregoing, no attempt has been made to consider the kinetics of the binding pairs of electrons. The success which has attended the application of the theories of Bohr and Sommerfeld to explain the spectral lines of hydrogen and helium inclines most physicists to the view that the electrons of atoms are rotating in orbits around positive nuclei. At a meeting of the Faraday Society in Cambridge, England, in July, Professor Sidgwick suggested that two atoms may be held together by two electrons rotating about the positive nuclei of the two atoms. A somewhat similar suggestion was made by the author some time ago.⁴ It is possible that some such hypothesis may ultimately be put on a sound basis and connected accurately with experimental facts, but at present it can be considered only as a very wild guess. It is somewhat in line with the theories

¹ G. H. Coleman, private communication.

² For reasons for believing that hypochlorous acid may easily separate into positive chlorine and negative hydroxyl, see Noyes and Wilson, This Journal, 44, 1630 (1922).

³ Noyes, Chem. News, 90, 228 (1904).

⁴ Noyes, This Journal, 39, 879 (1917).

of the physicists and it seems quite certain that at some future time our theories of chemical combination must be brought into harmony with the known facts about spectral lines, absorption bands, color and other phenomena of light and radiation.

CAMBRIDGE, ENGLAND Received September 4, 1923

WILLIAM A. NOVES

A Method for Reproducing Graphs in Quantity.—Graphs, etc., are plotted with waterproof india ink on the ordinary graph (or coördinate) paper. This is dipped in a saturated solution of purified, colorless paraffin oil (such as Stanolind-Liquid Paraffin) in chloroform and allowed to stand for  $^{1}/_{2}$  to 1 minute. It is then removed from the solution and allowed to drain as long as convenient. The excess of oil is wiped off and the sheet allowed to dry in the air until ready to use.

Using paper thus prepared, as a negative, photographic copies can be made on any of the bromide or blue print papers by direct printing. The bromide reproductions are particularly satisfactory and resemble photostats.

EVANS MEMORIAL BOSTON, MASSACHUSETTS Received September 14, 1923

W. C. GREENE R. S. HUNT

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

# THE BEHAVIOR OF MERCURIC SALTS OF ORGANIC ACIDS TOWARD HEAT

By Morris S. Kharasch² and Frederick W. Staveley³ Received October 28, 1922

In a previous communication Kharasch⁴ called attention to the fact that mercuric salts of certain aromatic carboxylic acids when heated split off carbon dioxide and the mercury becomes attached to the carbon originally bound to the carboxyl group. That reaction is applicable only to those aromatic carboxylic acids which split off carbon dioxide at their respective melting points or at slightly higher temperatures. In the case of the mercury salts of aromatic carboxylic acids, which do not split off carbon dioxide

- ¹ Read before the Organic Division of the American Chemical Society at the Pittsburgh Meeting, September, 1922.
  - ² National Research Fellow in Organic Chemistry.
- ³ The material presented here is used by F. W. Staveley in his dissertation presented in partial fulfilment of the requirements for the Degree of Doctor of Philosophy at the University of Chicago.
  - 4 Kharasch, This Journal, 43, 2238 (1921).

readily, the mercury usually becomes attached to a carbon of the benzene ring.  5 

The extent to which these reactions find their parallel in the aliphatic series has been the subject of an extensive investigation by Kharasch and various collaborators. The present communication deals primarily with the behavior toward heat of various substituted acetic acids. In selecting the compounds for this work, we were guided by the following considerations. We wanted to ascertain, first, the behavior toward heat of mercuric salts of substituted acetic acids not containing a replaceable hydrogen atom on the  $\alpha$  carbon atom; second, whether in phenylated acetic acids the velocity of mercuration of the benzene nucleus is greater than that of the  $\alpha$  carbon atom; third, the behavior of mercuric salts of substituted acetic acids that decompose readily into carbon dioxide and hydrocarbon.

The only work known to the writers which has been carried out on the behavior of mercuric salts of aliphatic acids toward heat is that of Dimroth.^{6,7} This author claims to have obtained a mercurated acetic acid by heating mercuric acetate, the reaction proceeding thus:

$$(H_3C.COO-)_2Hg \xrightarrow{\text{heat}} H_2C \cdot CO+H_3C.COOH$$
. It can also be stated with  $H_2C$ .

a fair degree of certainty that most of the mercury salts of aliphatic acids containing one or more hydrogen atoms on the  $\alpha$  carbon atom would behave in the same way, the mercury replacing one of the hydrogen atoms of the  $\alpha$  carbon atom. However, when the hydrogen atoms on the  $\alpha$  carbon atom are replaced by other groups, the reaction that takes place depends upon the character of the substituting radicals. Thus far, the investigation in this direction with salts of acids which do not split off carbon dioxide readily, has been confined to the study of various substituted acetic acids, namely, trimethyl-, trichloro-, phenyl-, diphenyl- and triphenylacetic acids.

In the case of the mercury salt of trimethylacetic acid, no change takes place when it is heated in a vacuum to 240° for 20 minutes, except that some of the salt distils. Thus, the salt still gives a precipitate of yellow mercuric oxide when treated with sodium hydroxide, and its behavior in other ways

 $^{^{5}}$  It is usually assumed that in substituted benzoic acids the mercury enters ortho to the carboxyl group. (See Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., 1921, p. 295, for references.) However, this is not rigidly correct. Thus, by heating the mercury salt of p-nitrobenzoic acid the mercury enters not only ortho to the carboxyl group, but also meta to it. This latter product has been overlooked by previous investigators.

⁶ Dimroth, Ber., 35, 2870 (1902).

⁷ The behavior of mercuric cyanide when heated is discussed later in the paper.

⁸ The mercury salts of methyl-, dimethyl- and ethylacetic acids have been found to give products of that type. They will be reported by one of us (Kh.) in connection with another investigation.

resembles that of mercury trimethylacetate. Similarly, when the salt is heated above its melting point in the air, no change can be detected by chemical means.

However, when all three hydrogen atoms of acetic acid are replaced by chlorine atoms, as in the case of trichloro-acetic acid, an entirely different reaction takes place. It must also be stated at the outset that our experience with the mercuric salt of trichloro-acetic acid is not in agreement with that of the previous investigator⁹ of this salt. We could not isolate the mercury salt by dissolving mercuric oxide in a water solution of trichloro-acetic acid, although it must have been formed, since the solution gave a precipitate of mercuric oxide when treated with sodium hydroxide. The solution of the salt, however, was found to be unstable and when heated, or concentrated in a vacuum, or even allowed to stand for any length of time, mercurous chloride separated, and carbon dioxide was evolved. 10,11

If we replace the hydrogen atoms in acetic acid by phenyl groups, instead of methyl or chloro, the decomposition reactions which the mercury salts undergo upon heating are different. Thus, when the mercury salts of phenyl- and diphenylacetic acids are heated slightly above their melting points, the mercury does not replace a hydrogen atom of the  $\alpha$  carbon atom, but one of the benzene ring. In that respect this reaction resembles the mercuration of aromatic acids by the dry heating of the salts of the latter compounds. In the case of triphenylacetic acid the reaction is more complicated; one of the products of the reaction is, however, a nucleus-mercurated triphenylacetic acid.  12  In no case is any product formed which contains the mercury on the  $\alpha$  carbon atom. It appears, thus, that in

⁹ Clermont, Compt. rend., 76, 774 (1874).

¹⁰ The reaction undoubtedly proceeds in two or more stages, the decomposition in the molecule beginning with the mercury oxidizing the carbon, and thus giving rise to

the following products:  $(Cl_3C.COO-)_2Hg \xrightarrow{12.0} 2$   $(Cl_3C.COOHg) + Cl_3C.COOH + (Cl_3C.OH) + CO_2$ . The trichlorocarbinol thus formed decomposed immediately into phosgene and hydrogen chloride. The decomposition of the former product in water then proceeds in the usual manner. The non-formation of chloroform in this reaction precludes the possibility that hexachloro-mercury dimethyl is an intermediate product in this reaction.

¹¹ This behavior of the mercuric salt of trichloro-acetic acid is somewhat similar to that of the mercuric salt of oxalic acid (from the electronic point of view the two acids are similar) since the mercuric salt of the latter acid when treated with ammonium chloride breaks down when warmed, into ammonium oxalate, carbon dioxide and mercurous chloride. [Souchay and Lennsen, Ann., 102, 42 (1857).] The ferric salt of oxalic acid is also known only in solution [Doberiner, Ann., 122, 113 (1862). Lemoine, Compt. rend., 116, 982 (1893)] and it decomposes very readily into ferrous oxalate and carbon dioxide. The behavior of the salts of these easily oxidizable acids is under investigation by one of us.

¹² This is most interesting in view of the fact that in pyridine solution the salt decomposes into triphenylmethyl and metallic mercury. See Ref. 4.

the case of phenylated acetic acids, the velocity of mercuration of the nucleus is much greater than that of the side chain. 13

From the considerations thus far developed it is quite evident what course the decomposition of a mercury salt of a substituted acetic acid of a given type would take. However, there is another factor involved in these decompositions, namely, the ease with which the acid loses carbon dioxide when heated. This is a very important factor, and the relative quantities of the products of the decomposition are largely dependent upon this factor. Of the acids thus far investigated, dimethyl- and diethylaceto-acetic acid and benzoylacetic acid might be mentioned. These acids were all selected because of their similarity, since all are substituted acetic acids, and lose carbon dioxide very readily. As anticipated, the mercuric salts of dimethyl- and diethylaceto-acetic acids when thoroughly dried and heated in a vacuum at 90° split off carbon dioxide, and the mercury became attached to the carbons originally bound to the carboxyl groups. This type of decomposition is illustrated below by that of the mercuric salt of

diethylaceto-acetic acid:  $[CH_3CO.C(C_2H_5)_2.CO_2]_2Hg \xrightarrow{\text{Heat}} 2CO_2 + [CH_3-CO.C(C_2H_5)_2-]_2Hg$ .

In the case of benzoylacetic acid, which contains two labile  $\alpha$  hydrogen atoms, the reaction may be made to go in either of two directions which depend upon the conditions under which the experiment is carried out. When the acid is heated with mercuric oxide in alcohol, carbon dioxide is evolved, and mercury-bis-benzoylmethane is obtained. If the reaction is carried out in chloroform, no carbon dioxide is lost, the mercury going to the  $\alpha$  carbon atom. The two processes may be illustrated by the following equations.

$$(C_6H_5COCH_2CO_2)_2Hg \xrightarrow{\text{heated}} 2CO_2 + (C_6H_5COCH_2)_2Hg$$

$$C_6H_5COCH-CO + C_6H_5COCH_2CO_2H$$

$$C_6H_5COCH-CO + C_6H_5COCH_2CO_2H$$

$$Hg-O$$

In the methylated and ethylated aceto-acetic acids, where the labile  $\alpha$  hydrogen atoms are replaced by alkyl groups, only the tendency to split off carbon dioxide was observed.

In the case of the acids previously mentioned where, upon heating the mercury salts, the mercury takes the place originally held by the carboxyl group, there is also a great tendency for the mercury to split out and link the two carbons. This usually takes place at temperatures slightly higher than those at which the decomposition of the mercury salt into the mercury-bis compound occurs although some compounds such as mercury-

13 The experimental data are not recorded in this paper, for the position of the mercury in the ring has not been definitely established, but will be reported in a later paper.

bis-acetodiethyl methane and the corresponding dimethyl compound lose mercury spontaneously when kept for a few days. Again, in the case of the mercuric salt of phthalide carboxylic acid, we were not able to isolate the intermediate mercury compound, the salt decomposing when heated into carbon dioxide, metallic mercury and dihydrophthalide. 14,15

CH—CO₂ heat 
$$(C_0H_4 O)_2Hg \xrightarrow{heat} Hg + 2CO_2 + C_0H_4 O O C_0H_4$$

Similar linking undoubtedly took place when the mercuric salts of diethyland dimethylaceto-acetic acids were distilled in a vacuum. The isolation of these ketones, and a thorough study of the linking of the carbon to carbon by means of these mercury derivatives will be continued by Kharasch and Mildred W. Grafflin.

Mercury carbon compounds differ very widely in their stability toward various reagents such as sodium hydroxide and ammonium sulfide. If we neglect, for the time being, the aromatic mercuri-organic derivatives, which will be discussed in greater detail in a paper by Kharasch and Chalkley, we may consider the mercury aliphatic compounds to be of the

¹⁴ An exceedingly interesting reaction takes place when the mercuric salt of phthalide carboxylic acid is treated with sodium hydroxide; metallic mercury separates and from the solution two acids can be isolated; phthalide carboxylic acid and its oxidation product phthalonic acid. It appears, thus, that in alkaline solution one-half of the phthalide carboxylic acid is oxidized to phthalonic acid, leading thus to the products isolated.

CH—CO₂

$$(C_6H_4 O )_2Hg + 3NaOH \longrightarrow Hg + 2H_2O + C_6H_4 O + C_6H_4$$

$$CO CO_2Na$$

$$CO CO_2Na$$

This rather striking behavior is very readily comprehended since phthalide carboxylic acid is a  $\gamma$  lactone, which we should expect to be quite susceptible to oxidation.

¹⁵ The chemistry of the decomposition of the keto carboxylic acid when heated will be reported by one of us in connection with the photochemical decomposition of mercuric salts of other keto acids, such as pyruvic acid.

¹⁶ The speed of reaction of bridged mercury compounds with mercuric chloride is also of great significance in regard to the stability of the mercury-carbon union in the bridged compounds. Mercury-bis-acetodiethyl and -dimethyl methane react almost instantly with mercuric chloride, in the following manner:  $[H_3C.CO.C(C_2H_5)_2-]_2$ -Hg + HgCl₂  $\longrightarrow$  H₃C.CO.C(C₂H₅).HgCl. The reaction of mercury-bis-acetodiethyl methane and mercuric chloride is taken for illustration. These compounds constitute the first definite mercury compounds of an alkylated acetone in which it is quite certain that the mercury is attached to a carbon atom. Some of the products of acetone, and substituted acetones, described in the literature are simply mixtures of various compounds, and there is absolutely no ground for assigning to a compound a formula such as the following:  $5(Me)_2CO.8HgSO_4.12HgO$  [Denigès, Ann. chim. phys. [8] 12, 401 (1907)]. It is merely an attempt on the part of the investigator to fit his analytical figures to a formula.

same kind as the inorganic compounds, but differing from them in being less ionized. Naturally, it is the degree of ionization of these derivatives that determines whether a compound will give a test with sodium hydroxide or ammonium sulfide. It is understood, of course, that the degree of ionization of the mercury from the carbon is a function of the constitution of the molecule. Thus, while mercuric chloride, a representative inorganic compound, gives an immediate precipitate of mercuric oxide when treated with sodium hydroxide, mercuric cyanide does not. Ammonium sulfide, however, precipitates mercuric sulfide from both substances, on account of the extraordinary insolubility of mercuric sulfide. Similarly, the mercury derivatives of substituted acetones, the bridged as well as the unbridged, do not give a test for mercuric ions with sodium hydroxide, but ammonium sulfide gives an immediate precipitate of mercuric sulfide. It is noteworthy in this connection that mercuric evanide and the bridged compounds, prepared from substituted acetoacetic acid, react very readily with mercuric chloride. Thus, soon after the solutions were mixed, sodium hydroxide failed in either case to give a test for mercuric ions. The reactions of these aliphatic mercury compounds thus parallel those of mercuric cyanide.

The decomposition of mercuric cyanide into metallic mercury and cyanogen when heated is also of great significance in this connection. It is merely an intramolecular oxidation-reduction reaction between the mercury and the carbon, and is thus quite similar to the decompositions which the aliphatic bridged mercury compounds, previously discussed, undergo when heated. The analogy in chemical behavior of mercuric cyanide and the bridged mercury aliphatic compounds indicates quite strongly that the former has a nitrile and not an isocyanide structure. This view also seems to be in accord with other facts known about mercuric cyanide. The notion certainly deserves consideration, in view of the facts advanced for its support, and will be more thoroughly discussed later.

The investigations along the various lines outlined in the paper are being continued at the University of Maryland.

# Experimental Part

Mercury-bis-benzoylmethane,  $(C_6H_6COCH_2)_2Hg$ .—To 1.3 g. of benzoylacetic acid dissolved in 50 cc. of 95% alcohol, 5 g. of yellow mercuric oxide was added. The whole was then heated to boiling, and filtered. The residue was boiled with 20 cc. of alcohol and filtered. The two filtrates were combined, diluted with water, and cooled in an icebath. A faintly yellow precipitate separated which was washed with water and dried on a porous plate; m. p., 159.5°; yield, 0.8 g.

Analysis.  17  Subs., 0.2624: HgS, 0.1386. Calc. for  $C_{16}H_{14}O_{2}Hg$ : Hg, 45.72. Found: 45.56.

The compound is white. It is soluble in hot alcohol and crystallizes as the solution cools. It is soluble in acetone but insoluble in water or ether.

¹⁷ Unless otherwise indicated all samples for analysis were dried to constant weight in a vacuum over sulfuric acid.

An alcoholic solution of the compound does not give mercuric oxide when treated with sodium hydroxide; however, ammonium sulfide gives an immediate precipitate of mercuric sulfide.

When mercury-bis-benzoylmethane is treated with mercuric chloride it forms the compound described immediately below.

Benzoylmethyl-mercuric Chloride,  $C_6H_5COCH_2HgCl$ .—To 0.32 g. of mercury-bis-benzoylmethane, dissolved in 10 cc. of hot 95% alcohol, 0.2 g. of mercuric chloride was added, and the mixture heated on the water-bath until it no longer gave a test for mercuric ion when sodium hydroxide was added. It was then diluted with water and cooled in ice. The precipitate was collected on a filter, washed with water, and dried on a porous plate; m. p.,  $146^\circ$ ; yield, 0.3 g. The compound thus obtained was found to be identical with that prepared by direct mercuration of acetophenone, the constitution of which has been definitely established as benzoylmethyl-mercuric chloride (phenacylmercuric chloride).

Anhydro- $\alpha$ -hydroxy-mercuribenzoyl Acetic Acid, C₀H₃CO—CH—CO—O—Hg.—

An excess of yellow mercuric oxide was added to 3 g. of benzoyl-acetic acid dissolved in 50 cc. of chloroform. The mixture was kept at the boiling temperature of chloroform for a minute and then filtered. When the filtrate was evaporated to dryness a white solid remained. To remove unchanged benzoylacetic acid, the product obtained above was extracted twice with ether. It was then dried in a vacuum over sulfuric acid; yield, 1.3 g.

Analysis. Subs., 0.4706: HgS, 0.3027. Calc. for  $C_0H_6O_3Hg$ : Hg, 55.32. Found: 55.47.

The compound is white. It is slightly soluble in cold chloroform, very soluble in hot, and insoluble in ether; it is insoluble in water, but readily soluble in sodium hydroxide. The compound decomposes at about 290°. When treated with dil. hydrochloric acid, benzoylacetic acid and mercuric chloride are formed. The compound does not give an immediate violet coloration with an alcoholic ferric chloride solution but, if it is first acidified with hydrochloric acid, an immediate violet coloration characteristic of benzoylacetic acid is obtained.

Mercuric Phthalide-Carboxylate, (CoH4COOCHCOO)2Hg.—To 1 g. of phthalide

carboxylic acid, dissolved in 200 cc. of hot water, 0.89 g. of mercuric acetate, dissolved in a small amount of water, was added. A heavy white precipitate was obtained which was collected on a filter, washed with cold water and then with a small amount of alcohol and ether. It melted, with decomposition, at 195°.

Analyses. Subs., 0.3277, 0.5667, 0.4674: HgS, 0.1380, 0.2336, 0.1942. Calc. for  $C_{18}H_{10}O_{3}Hg$ : Hg, 36.16. Found: 36.32, 35.55, 35.83.

The compound is easily soluble in hot acetone and insoluble in cold alcohol and ether. When it is treated with sodium hydroxide, metallic mercury separates.

## Action of Sodium Hydroxide on the Mercuric Salt of Phthalide Carboxylic Acid

To 5 g. of mercuric phthalide carboxylate 10 cc. of sodium hydroxide (6 N) was added. An immediate precipitation of metallic mercury took place. The mixture was filtered and the filtrate shaken with charcoal, to remove traces of finely divided mercury, and then filtered again. After that, the filtrate did not contain any mercury. It was acidified with dil. sulfuric acid and extracted several times with ether. On evaporation of the ether an oil was obtained which solidified after standing for some time. The compound was easily soluble in water; m. p.,  $100^{\circ}$ ; yield, 1.2 g. The compound thus

obtained was extracted with chloroform and the insoluble portion was treated with a very small amount of water and allowed to crystallize slowly, after which the crystals were again extracted with chloroform. The residue dried on a porous plate, melted at 140°. Phthalonic acid prepared by the oxidation of naphthalene melted at 145°, and a mixture of the phthalonic acid with the above product melted at 140°. Both products gave a red coloration when treated with coned. sulfuric acid and benzene containing thiophene.

The chloroform filtrates were combined, evaporated to dryness, and the solid residue was extracted twice with small amounts of water. The residue was dried on a porous plate. This product melted at 144.5°. Phthalide carboxylic acid prepared by reducing phthalonic acid melted at 151°, and a mixture of the two melted at 150°. This product gave only a faint pink coloration with concd. sulfuric acid and benzene containing thiophene.

When mercuric-phthalide carboxylate is heated to 195°, it melts and decomposes, metallic mercury separates and the compound described immediately below is formed.

## Preparation of Dihydrophthalide from the Mercuric Salt of Phthalide Carboxylic Acid

One g. of the well-dried mercuric salt of phthalide carboxylic acid was heated to 195° when it decomposed with the separation of metallic mercury. When cold the solid was extracted with hot glacial acetic acid. As the filtrate was cooled, a yellow solid separated which was collected on a filter and washed with water. The product was then dried in a vacuum over sulfuric acid; m. p., 250°; yield, 0.36 g.

Pure dihydrophthalide prepared from phthalic anhydride, mixed with this compound was found not to depress the melting point.

Mercurous Benzoylformate,  $C_6H_6CO.CO_2Hg.$ —Benzoylformic acid was dissolved in 175 cc. of 80% alcohol, and 40 g. of yellow mercuric oxide was added. The mixture was boiled for a few minutes and filtered. As the filtrate cooled, a white precipitate separated which was collected on a filter.

Analysis. Subs., 0.1597: HgS, 0.1063. Calc. for C₈H₅O₅Hg: Hg, 57.40. Found: 57.45.

The compound is white. When it is treated with sodium carbonate or sodium hydroxide, metallic mercury separates. The same observation was made when pyridine was used as a solvent for the compound. This is characteristic of mercurous salts. The compound is only slightly soluble in boiling alcohol. When acidified with dil. sulfuric acid and extracted with ether, the ether extract upon evaporation gave a white solid which melted at 57°. Benzoylformic acid melts at 62° and was found not to depress the melting point of this compound. When the substance was heated the odor of benzaldehyde was noticeable.

Mercuric Benzoylformate, (C₆H₅CO.CO₂)₂Hg.—To 12.6 g. of benzoylformic acid dissolved in 500 cc. of water, a solution of 13.4 g. of mercuric acetate in 100 cc. of water was added slowly and the mixture was constantly stirred. A white precipitate was obtained which was collected on a filter and washed with water; m. p., 164°; yield, 15 g.

Analysis. Subs., 0.1779: HgS, 0.0867. Calc. for  $C_{16}H_{10}O_6Hg$ : Hg. 40.23. Found: 42.03.

The compound is white. It is soluble in pyridine and nitrobenzene, but only slightly soluble in water. When it was heated to 180° mercury separated, carbon dioxide was evolved and benzoic acid was formed. After it had been refluxed in nitrobenzene, a solid was obtained which had no definite melting point but decomposed at about 200°, and when treated with sodium hydroxide or pyridine metallic mercury separated from it. This is characteristic of mercurous salts.

Mercuric- $\alpha$ , $\alpha$ -diethyl-aceto-acetate, [CH₃CO.C(C₂H₅)₂.CO₂]₂Hg.—To 8.5 g. of  $\alpha$ , $\alpha$ -diethyl-aceto-acetic acid, dissolved in 50 cc. of 30% alcohol, 9.2 g. of mercuric acetate, dissolved in a small amount of water, was slowly added and the mixture constantly stirred. The precipitate was collected on a filter, washed with water and then with a small amount of alcohol. The product thus obtained melted at 103° with decomposition; yield, 7 g.

Analysis. Subs., 0.1649: HgS, 0.0754. Calc. for  $C_{16}H_{26}O_{6}Hg$ : Hg, 38.97. Found: 39.43.

The compound is easily soluble in pyridine and hot alcohol. It is not very soluble in ether or cold nitrobenzene but dissolves in hot nitrobenzene, metallic mercury separating at the same time. When the compound is heated to its melting point carbon dioxide is evolved and the product described immediately below is formed.

Mercury-bis-aceto-diethylmethane,  $(CH_3CO.C(C_2H_5)_2-)_2Hg$ .—When mercuric- $\alpha$ ,  $\alpha$ -diethyl-aceto-acetate was heated in a vacuum to 85°, the compound melted, carbon dioxide was evolved and later the melt solidified. When the loss in weight corresponded to two molecular equivalents of carbon dioxide, the reaction was considered complete. The solid was then dissolved in acetone and the solution filtered. Upon slow evaporation of the solvent, a white solid separated which was dried on a porous plate. It melted at  $109^{\circ}$  with decomposition. The yield was almost quantitative.

For analysis the compound was dried as quickly as possible in a vacuum over phosphorus pentoxide.

Analysis. Subs., 0.1319: HgS, 0.0736. Calc. for  $C_{14}H_{26}O_2Hg$ : Hg, 47.00. Found: 48.11.

The compound is soluble in acetone, chloroform and benzene, but insoluble in water. It is unstable and decomposes rapidly, with the separation of metallic mercury, into an oil which has an odor somewhat resembling that of camphor. This instability explains the high value obtained for mercury. When an alcoholic solution of the compound was treated with ammonium sulfide a precipitate of mercuric sulfide was formed immediately.

When this substance is treated with mercuric chloride, the compound described immediately below is formed.

Aceto-diethyl-methyl-mercuric Chloride,  $(CH_3CO.C(C_2H_3)_2-)HgCl.-To$  1.75 g. of mercury-bis-aceto-diethylmethane dissolved in 15 cc. of 95% alcohol was added a solution of 1.12 g. of mercuric chloride in 30 cc. of warm alcohol. The solution was cooled in a freezing mixture, and a white solid separated; m. p., 77°; yield, 0.85 g.

Analysis. Subs., 0.3618: HgS, 0.2408. Calc. for  $C_7H_{13}$ OClHg; Hg, 57.44. Found: 57.40.

The compound crystallizes slowly from alcohol. In the above preparation, shortly after the mercuric chloride was added to the mercury-bis-aceto-diethylmethane, no mercuric ions could be detected by the addition of sodium hydroxide. The compound gave, however, an immediate precipitate of mercuric sulfide with ammonium sulfide.

Mercuric Dimethyl-aceto-acetate,  $[CH_2CO.C(CH_8)_2.CO_2]_2Hg.$ —To 40 g. of mercuric acetate dissolved in 150 cc. of water was slowly added 29 g. of  $\alpha,\alpha$ -dimethylaceto-acetic acid, dissolved in 100 cc. of 30% alcohol. A thick paste formed immediately. More water was then added and the mixture was well stirred; the precipitate was collected on a filter and washed well with water. When dried on a porous plate the compound melted at 100°, with decomposition; yield, 15.5 g.

Analysis. Subs., 0.4237: HgS, 0.2206. Calc. for C₁₂H₁₈O₆Hg: Hg, 43.74. Found: 44.80.

The compound is white and is insoluble in water. When heated to 100°, it melts with decomposition, carbon dioxide is evolved and metallic mercury separates. With

sodium hydroxide a yellow precipitate of mercuric oxide is obtained. When it is heated to 90° in a vacuum, the product does not melt but carbon dioxide is evolved and the compound described immediately below is formed.

Mercury-bis-aceto-dimethyl-methane,  $[CH_3CO.C(CH_3)_2-]_2Hg.$ —When mercuric  $\alpha,\alpha$ -dimethyl-aceto-acetate was heated in a vacuum at 90° it lost two molecular equivalents of carbon dioxide as indicated by an equivalent loss in weight. The solid was then extracted with acetone at room temperature and the acetone evaporated in a vacuum over sulfuric acid. A white solid remained which melted at 120° with decomposition. The yield was almost quantitative.

For analysis the compound was dried as rapidly as possible in a vacuum over phosphorus pentoxide.

Analysis. Subs., 0.3355: HgS, 0.2094. Calc. for  $C_{10}H_{18}O_2Hg$ : Hg, 54.11. Found: 53.83.

The compound is soluble in acetone and alcohol, and very slightly soluble in ether. It may be crystallized from toluene or xylene. No mercuric oxide formed upon the addition of sodium hydroxide, but upon the addition of ammonium sulfide an immediate precipitate of mercuric sulfide was obtained. The compound is unstable and rapidly decomposes with the separation of metallic mercury. When the compound (5 g.) was distilled in a vacuum at 90°, 1.3 g. of an oil was obtained which gave only a faint test for mercury and had an odor resembling that of camphor.

When mercury-bis-aceto-dimethyl-methane is treated with mercuric chloride the product described below is formed.

Aceto-dimethyl-methyl-mercuric Chloride, CH₃CO.C(CH₃)₂—HgCl.—A solution of 1.4 g. of mercuric chloride dissolved in 30 cc. of 95% alcohol was added to 1.8 g. of mercury-bis-aceto-dimethyl-methane in 15 cc. of alcohol. The mixture was refluxed for five minutes. As it cooled, beautiful white crystals with a metallic luster separated; m. p., 124.5°; yield, 1.1 g.

Analyses. Subs., 0.3127, 0.2934: HgS, 0.2229, 0.2116. Calc. for  $C_6H_9OClHg$ : Hg, 62.49. Found: 61.48, 62.20.

The compound is soluble in hot alcohol. When treated with sodium hydroxide it does not give a precipitate of mercuric oxide, but ammonium sulfide gives an immediate precipitate of mercuric sulfide.

Mercuric Trimethylacetate, [(CH₃)₃C.CO₂]₂Hg.—Trimethylacetic acid was dissolved in sodium hydroxide and the calculated amount of mercuric nitrate was added. A yellow product separated which was purified by crystallization from hot chloroform. Long, beautiful white needles were thus obtained which melted at 235°. The yield was good.

Analysis. Subs., 0.2855: HgS, 0.1629. Calc. for  $C_{10}H_{18}O_4Hg$ : HgS, 49.81. Found: 49.21.

The compound is soluble in hot chloroform and pyridine, but is very slightly soluble in carbon tetrachloride. When it was boiled in nitrobenzene, the color of the solution gradually became darker and metallic mercury separated. When it was heated to 240° in a vacuum, there was no evolution of carbon dioxide.

#### The Action of Mercuric Oxide on Trichloro-acetic Acid

1. Freshly distilled trichloro-acetic acid was dissolved in water and treated with an excess of yellow mercuric oxide and the solution filtered. When the filtrate was allowed to stand at room temperature (or concentrated in a vacuum) a mercurous salt was formed, as proved by the fact that it gave a precipitate of metallic mercury when treated with sodium hydroxide or pyridine. This mercurous salt is mercurous chloride, as is shown by the following analysis.

Analysis. Subs., 0.6908: HgS, 0.6647. Calc. for HgCl: Hg, 84.96. Found: 82.99.

When the filtrate from trichloro-acetic acid and mercuric oxide was heated to  $60-65^{\circ}$ , mercurous chloride precipitated and the acidity of the solution increased and reached a constant value after 30 minutes; at the end of that time all of the mercuric salt originally present had been converted into mercurous chloride.

2. A chloroform solution of freshly distilled trichloro-acetic acid was treated with yellow mercuric oxide containing a little water and the insoluble portion collected on a filter. The filtrate upon evaporation gave a white solid which was identified as mercuric chloride. Mercurous chloride was identified as part of the insoluble portion.

### Summary and Conclusions

- 1. The behavior of mercury salts of various aliphatic carboxylic acids which do not lose carbon dioxide when heated has been studied. In cases where there is a replaceable hydrogen on the  $\alpha$  carbon atom, the mercury usually takes that position, giving an inner anhydride.
- 2. The abnormal behavior of the mercury salt of trichloro-acetic acid has been pointed out.
- 3. In the case of the mercury salts of phenylated acetic acids the velocity of mercuration in the benzene nucleus was found to be greater than that of the  $\alpha$  carbon atom—so that in working with 15- or 20g. lots, no side chain substitution products could be isolated.
- 4. In the case of mercury salts of substituted aliphatic acids which split off carbon dioxide readily, the mercury usually takes the place previously occupied by the carboxyl groups, thus linking the two molecules. (See the behavior of benzoylacetic acid for the possibilities of side reactions.)
- 5. The substituted mercury acetone derivatives, the bridged as well as unbridged, do not react with sodium hydroxide, but give an immediate precipitate of mercuric sulfide when treated with ammonium sulfide. Their behavior is similar to that of mercuric cyanide.
- 6. It is pointed out that the evidence is more in favor of a nitrile structure for mercuric cyanide than an isocyanide structure.
- 7. The linking of carbon to carbon through the intermediate mercuribis compounds is discussed, and the formation of dihydrophthalide from mercuric-phthalide-carboxylate is considered in the light that it is merely a case of intramolecular oxidation-reduction in which the mercury acts as the oxidizing agent.
- 8. The oxidation of a  $\gamma$  lactone to a ketonic acid by the use of mercuric oxide in alkaline solution has been observed.
- 9. The preparation of the following new compounds is described: mercury-bis-benzoylmethane; anhydro- $\alpha$ -hydroxymercuri-benzoyl-acetic acid; mercuric phthalide-carboxylate; mercurous benzoylformate; mercuric benzoylformate; mercuric  $\alpha,\alpha$ -diethyl-aceto-acetate; mercury-bis-aceto-diethylmethane; aceto-diethyl-methyl-mercuric chloride; mercuric  $\alpha,\alpha$ -

dimethyl-aceto-acetate; mercury-bis-aceto-dimethylmethane; aceto-dimethyl-methyl-mercuric chloride; mercuric trimethylacetate.

College Park, Maryland

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# NEW METHODS OF SPLITTING PYRIMIDINES. II. THE DECOMPOSITION OF PYRIMIDINES BY MEANS OF FERROUS SALTS

By Mimosa Hortense Pfaltz¹ and Oskar Baudisch Received February 1, 1923

The reactions which we have used in splitting pyrimidines take place under conditions resembling as closely as possible natural conditions in the metabolism of plants and animals. Two methods have been studied intensively, namely, the system, ferrous sulfate plus sodium bicarbonate plus air, and the system, sodium pentacyano-aquo-ferroate,  2  [Fe  $^{\rm II}(\rm CN)_5\rm OH_2$ ]Na3, plus oxygen or air. In both cases the reactions were carried out at room temperature (primary process), while the complete hydrolysis of the intermediate products (secondary process) was brought about at blood-temperature or at the temperature of the water-bath.

These methods, which were introduced by Baudisch,³ will be applied to other types of compounds. The use of the system, ferrous sulfate plus sodium bicarbonate plus air, in a very sensitive test for thymine has already been described.⁴

Ferrous salts, which have been used previously only as reducing agents, under suitable conditions exert a strong hydrolyzing and oxidizing action on certain types of compounds. The reactions in the cases which have already been studied are quite similar to the hydrolytic changes brought about by life processes or by light energy. Under mild conditions it is possible to cause a partial hydrolysis of the stable pyrimidine ring with the formation of substances which are completely hydrolyzed by sodium bicarbonate at temperatures between 37° and 80°.

# The Action of Ferrous Sulfate Plus Sodium Bicarbonate Plus Air on Pyrimidines

When ferrous sulfate is added to an aqueous solution of uracil containing an excess of sodium bicarbonate, a green ferrous carbonate peroxide is precipitated. When the reaction mixture is shaken with air, the ferrous compound is oxidized gradually to ferric hydroxide, while the pyrimidine

- ¹ This paper is constructed from a dissertation presented by Mimosa Hortense Pfaltz to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy. (O. B.)
  - ² Hofmann, Ann., 312, 1 (1900).
  - ³ Baudisch, Ber., 54, 406 (1921).

Johnson and Baudisch, This Journal, 43, 2670 (1921); Ber., 55, 18 (1922).

suffers a partial hydrolysis with the formation of an intermediate compound. When the filtered solution, which contains excess sodium bicarbonate, is warmed this intermediate compound is completely hydrolyzed to urea and other products. When thymine is used instead of uracil, we obtain urea, acetol and pyruvic acid.

The amount of bicarbonate in the solution affects the extent of the hydrolysis.

# Table I Influence of Bicarbonate and Evaporation

In each experiment 2.0 g. of uracil, 30 g. of FeSO₄.7 $\rm H_2O$ , and 700 cc. of distilled water were used. The reaction mixture, after the addition of solid NaHCO₂, was shaken with air in a flask.

Weight of NaHCOs		% Urea formed		
G.	Molecular equivalents	Without evaporation	With evaporation	
18	2	0	0	
54	6		$7.43^{a}$	
108	12 .	traces	12.1	

^a The numerical values for urea do not take into account the slight hydrolysis produced by the distillation with sodium bicarbonate.

# The Action of Sodium Pentacyano-aquo-ferroate Plus Oxygen or Air on Pyrimidines

The system, sodium pentacyano-aquo-ferroate² ("aquo salt")⁵ plus oxygen or air, also brings about a partial hydrolysis of the pyrimidine ring. Four-tenths g. of uracil and 1.00 g. of the complex salt were dissolved in distilled water and a stream of oxygen gas was passed through the solution for 16 hours. Urea could not be detected in the reaction mixture, even after it was warmed on the water-bath. However, after the addition of sodium bicarbonate and evaporation, a quantity of urea was found which corresponded to a split of 6.43%.

The quantity of uracil split can be increased by shaking the dark green solution of uracil and aquo salt with oxygen under a pressure slightly greater than one atmosphere.

Table II

Influence of "Activation" and Oxygen Pressure
In each experiment 0.200 g, of uracil and 0.60 g, of aquo salt were used.

No.	Conditions	Urea formed
1	Uracil with stream of oxygen for 22 hours	18.3
2	"Activated uracil" with stream of oxygen for 22 hours	15.5
3	"Activated uracil" shaken with oxygen under pressure for 10	
	hours	53.0

Evidence will be submitted below for the assumption that a loose compound is formed by uracil and aquo salt, the presence of this compound

^{5 &}quot;Aquo salt" is used for convenience as an abbreviation for sodium pentacyanoaquo-ferroate.

being indicated by a strong green color; when present in this compound, uracil may be said to be activated. In Expt. 3, oxygen displaces the uracil more readily from the compound because of the greater pressure. This oxygen enters the inner sphere of the complex salt and thus becomes activated with the result that it is able to react with activated uracil.

The largest splits are obtained when a freshly prepared solution of aquo salt and uracil is shaken with oxygen under slight pressure. Under these conditions amounts of urea up to 57% of that calculated were found.

It should be emphasized that the presence of ferrous salts is necessary to bring about a decomposition of pyrimidines by the action of molecular oxygen under ordinary conditions. This fact was proved by experiments in which oxygen was passed through aqueous solutions of uracil and thymine for 22 hours. Solid sodium bicarbonate was then added and the solutions were evaporated to dryness. By careful tests with xanthydrol it was impossible to detect any trace of urea.

## The Action of Ferrous Sulfate Plus Oxygen and of Ferrous Sulfate Plus Hydrogen Peroxide on Pyrimidines

If oxygen is passed through a solution of uracil or thymine containing ferrous sulfate, only a small split results. The extent of the split is slightly greater if hydrogen peroxide is substituted for oxygen. As stated above, the presence of a ferrous salt is necessary for the decomposition when molecular oxygen is used.

#### TABLE III

Comparison of Activation of Oxygen by Simple and Complex Iron Salts

In each experiment 0.200 g. of pyrimidine and an equimolecular quantity of the ferrous salt were used. The uracil solutions were shaken 11.5 hours with oxygen under pressure and the thymine solutions 24 hours.

Reagent	Urea formed	Urea formed
Oxygen	. 0	0
Aquo salt + oxygen	. 40.9	13.1
$FeSO_4.7H_2O + H_2O_2$	. 4.3	3.5
FeSO _{4.7H₂O + oxygen}	. 2.9	2.0

# Evidence of Compound Formation between Complex Ferrous Ions and Pyrimidines

An explanation of the action of aquo salt as a catalyst in the reactions which have been discussed can best be given by considering the process in the light of Werner's Coördination Theory.

- ⁶ An aqueous solution of aquo salt is light yellow in color, while an aqueous solution of uracil is colorless.
- ⁷ It has been shown by Bass, however, that oxygen is able to split thymine to some extent under the influence of light, even in the absence of ferrous salts. L. W. Bass, This Journal, 1924.

It has been shown that sodium pentacyano-aquo-ferroate can form compounds in which aquo (water molecule) has been replaced by whole organic molecules, such as pyridine, nitrosobenzene, p-nitrosodimethylaniline, etc.

Most of these "penetration compounds" are characterized by their striking colors. For example, in the reaction given above the light yellow color of the aquo salt changes to deep violet. The nitrosobenzene can be displaced from this violet compound by other substances which have a stronger affinity for the iron nucleus, such as sodium nitrite, sodium cyanide and carbon monoxide. In other words, we have to do with a competition for the auxiliary valences of the complex nucleus.

By analogy we are led to the conclusion that the pyrimidines, also, in the reaction with aquo salt primarily become linked to the central iron atom by displacing the water molecule. This conclusion is justified by the striking color changes which take place when a pyrimidine is allowed to react with aquo salt in the absence of air. Uracil and thymine form dark green compounds, while cytosine yields a deep red compound.

As a result of this compound formation the pyrimidine becomes "activated" and is therefore more susceptible to hydrolysis and oxidation. Similarly, oxygen becomes "activated" by other molecules of the complex salt.

While we have definite evidence, in the case which has just been discussed, of the dependence of the reaction upon the auxiliary valences of the iron nucleus, we have no conclusive proof that penetration compounds containing pyrimidines are formed by ferrous carbonate or its peroxide. In this case, however, it was proved indirectly that addition of the pyrimidine to ferrous ion precedes the reaction; hence, we believe that this reaction also is dependent upon the action of auxiliary valences.

If caustic alkali is used in place of the weakly alkaline bicarbonate, the freshly precipitated ferrous hydroxide is able to absorb and activate atmospheric oxygen, but the pyrimidine present is not split under these conditions because the sensitive auxiliary valences of the ferrous ions are already occupied by sodium hydroxide molecules which the pyrimidine is unable to displace. If more alkali is used, even the absorption of oxygen

⁸ Manchot and Woringer, Ber., 46, 3519 (1913).

⁹ Ref. 3, p. 414.

¹⁰ Schwarz-Bass, "The Chemistry of the Inorganic Complex Compounds," John Wiley and Sons, New York, 1923, p. 30.

is prevented,¹¹ that is, the precipitate of ferrous hydroxide remains white even when oxygen is passed through the reaction mixture.

Additional proof of the assumption that the reaction depends upon the action of auxiliary valences has been brought forward by Bass, 12 who has shown that the catalytic decomposition of pyrimidines by the system, ferrous sulfate plus sodium bicarbonate plus air, may be poisoned by adding small quantities of arsenic trioxide, potassium nitrite, or ammonia to the reaction mixture.

#### Methods of Retarding the Reaction

The hydrolytic split of pyrimidines by aquo salt plus oxygen can be retarded in two ways. First, substances can be added to the reaction mixture which have a strong affinity for iron and which, therefore, occupy the auxiliary valences of the iron nucleus (poisoning). Second, the pyrimidine ring can be transformed into a more saturated condition, thus retarding or even preventing the formation of a complex compound with the ferrous salt.

In the first case the reaction may be retarded by adding potassium cyanide to the reaction mixture in an amount equivalent to the aquo salt and by allowing the solution to stand for a few minutes before passing in oxygen. When a solution of 0.200 g. of uracil and 0.60 g. of aquo salt was treated with oxygen for 22 hours, a quantity of urea equivalent to a split of 18.3% was obtained. In a duplicate experiment with an equimolecular quantity of potassium cyanide (0.155 g.), only 2.05% of urea was formed. Ammonia may be used in place of potassium cyanide. In an experiment with sodium pentacyano-ammine-ferroate, [Fe^{II}(CN)₅NH₃]-Na₃, uracil was not attacked, while a duplicate experiment with aquo salt gave a split of 9.7%.

When uracil, in complete absence of air, is shaken with aquo salt, we obtain the deep green solution mentioned previously, which has been shown to contain a complex compound of uracil and aquo salt. If oxygen is passed through this solution, only a small quantity of urea is formed, a fact which indicates that oxygen is not activated by the complex compound.

The second method of retarding the reaction, saturation of the pyrimidine ring, is best illustrated by comparing the extent of the split in uracil and hydro-uracil. In each experiment we used  $0.200~\rm g$ . of pyrimidine with an equimolecular quantity of aquo salt, the solution being shaken with oxygen under pressure for 9 hours. Under these conditions uracil gave 31.9% of urea and hydro-uracil 12.3%. From these results it is seen that saturation of the double bond in uracil decreases the extent of the split.

¹¹ Baudisch and Mayer, Biochem. Z., 107, 1 (1920).

¹² Bass, unpublished researches.

# The Influence of the Methyl Group on the Stability of the Pyrimidine Ring

The influence of the methyl group on the stability of the pyrimidine ring under the conditions which we have described is illustrated by the following results. In experiments using 0.200 g. of pyrimidine, an equimolecular quantity of aquo salt, and oxygen under pressure, the following splits were obtained: uracil, 31.9%; thymine, 14.7%; and 4-methyluracil, 55.6%.

It has been shown by Biltz¹³ that in alkaline solution carbon atom 5 of alloxan has a strong affinity for one of the nitrogen atoms of the urea residue and that under suitable conditions alloxanic acid is formed.

This property can undoubtedly be shared by other pyrimidines and explains the fact that thymine is more stable than uracil or 4-methyluracil. In thymine a methyl group is linked to the sensitive carbon atom in Position 5, with the result that any reactions attacking this carbon will be hindered. In 4-methyluracil, on the other hand, the methyl group is attached to a carbon atom which does not have a direct influence on the reaction.

#### Experimental Part

Apparatus.—For the precipitation of ferrous hydroxide in the absence of air an 800cc. Kjeldahl flask was used which was provided with a ground-glass stopper fused to a glass tube ending in a glass stopcock. The same type of flask was used in experiments which were conducted by shaking the reaction mixtures with oxygen under pressure. In experiments which employed a stream of oxygen, small gas wash bottles of about 300 cc. capacity were used.

### Analytical Methods

Urea Determination.—Urea determinations were made in the filtered solutions obtained by dissolving with water the dry residues resulting from the evaporation of the reaction mixtures with sodium bicarbonate. The urea was precipitated according to Fosse's directions for solutions containing from 0.1 g. to 1.0 g. of urea per liter. The proportions are 1 volume of solution, 2 volumes of glacial acetic acid, and 1/20 volume of a 10% solution of xanthydrol in methyl alcohol.

To insure complete precipitation, the solutions were usually allowed to stand overnight. The precipitate was filtered in a Gooch crucible and was washed first with alcohol to remove excess of xanthydrol and then with water until free from acid. After the addition of glacial acetic acid the solutions always turned green when pentacyano salts had been used. This Prussian blue was removed from the precipitates by washing them

¹³ Biltz, Heyne and Bergius, Ann., 413, 68 (1916). Biltz, Ber., 54, 1809 (1921).

¹⁴ Fosse, Ann. chim., [9] 6, 13 (1916).

first with water and then with alcohol. The crucibles were dried at 120° and the dixanthylurea was identified by its melting point (257°).

Acetol Test.—Acetol tests were made on the clear distillates obtained from reaction mixtures of thymine. The test depends upon the formation of 3-hydroxy-quinaldine when acetol is treated with o-aminobenzaldehyde in alkaline solution.¹⁵ This compound shows a strong blue fluorescence, a phenomenon which makes the test very delicate.

The heated distillate from the reaction mixture was treated with 0.01 g. of o-amino-benzaldehyde in alcohol and 5 cc. of sodium hydroxide. Two-thirds of this solution was evaporated by boiling. After cooling, it was acidified with hydrochloric acid and then made alkaline with an excess of solid sodium bicarbonate. A blue fluorescence proved the presence of acetol. If the test obtained was so slight as to be doubtful, some of the solution was poured into a quartz test-tube and illuminated by ultraviolet light from an iron arc. By this means a test was often obtained when the blue fluorescence was not visible in daylight.

Pyruvic Acid Test.—This test was applied to the residues obtained by evaporating thymine reaction mixtures to dryness. It depends upon the formation of indigo when pyruvic acid in alkaline solution is treated with o-nitrobenzaldehyde. 16

After evaporation of the reaction mixture the residue was taken up with water and evaporated again almost to dryness. To this solution were added an aqueous emulsion of o-nitrobenzaldehyde and a small quantity of potassium hydroxide solution.

The mixture was then shaken with chloroform. A deep blue color in the chloroform layer proved the presence of pyruvic acid in the sample.

#### Experiments with Ferrous Carbonate Peroxide

The discussion of the experimental work with ferrous carbonate peroxide will be confined to a complete description of one typical experiment.

Two g. of uracil (Expt. 2, Table I) were dissolved with 54 g. of sodium bicarbonate in 700 cc. of boiling water. This solution was boiled for at least one hour in an 800cc. Kjeldahl flask (as described above) to remove all oxygen dissolved in the water. A test-tube containing 30 g. of powdered ferrous sulfate (FeSO₄.7H₂O) was lowered into the flask and the contents were boiled for 10 minutes longer. The ground-glass stopper, with the stopcock open, was fitted into the neck. When steam began to come out of the open end of the stopper the flame was removed and the stopcock was closed. After the reaction mixture had been cooled to room temperature the flask was inverted so that the alkaline uracil solution came into contact with the ferrous sulfate. A grayish-white precipitate of ferrous carbonate was formed, which slowly hydrolyzed to ferrous hydroxide.

When all of the ferrous sulfate had dissolved, the stopcock was opened to admit air. The precipitate of ferrous hydroxide immediately darkened and then turned green rapidly as the flask was shaken because of the formation of ferrous carbonate (or hydroxide) peroxide. The contents of the flask were then poured into a 2-liter round-bottom flask fitted with a rubber stopper containing a bent glass tube. This flask was shaken by hand until all the ferrous hydroxide peroxide had become oxidized to ferric hydroxide, a process which required about  $1^1/2$  hours.

When the oxidation was completed the reaction mixture was poured into a 1-liter graduated cylinder to allow the precipitate to settle. The clear supernatant liquid began to turn deep red, the color appearing first at the surface and spreading slowly downward through the liquid. After the liquid had stood overnight, the color varied

¹⁵ Baudisch, Biochem. Z., 89, 279 (1918). Compare Ref. 4.

¹⁶ Baeyer, Ber., 15, 2856 (1882). Compare Ref. 4.

from light to dark red, being darkest at the surface. This fact indicated that an absorption of oxygen had taken place, probably by the complex iron salts which exist in the solution.¹⁷

The volume was then made up to 650 cc. and two portions of 50 cc. each were removed by a pipet for determination of urea. One of these portions was evaporated to dryness before the analysis. (For results see Table I.)

#### Experiments with Sodium Pentacyano-aquo-ferroate

In this case, also, only one typical experiment will be described in detail.

One g. of uracil was dissolved in about 400 cc. of boiling water and the solution was then cooled to room temperature and diluted to 500 cc. One hundred cc. of this solution was transferred with a pipet to a Kjeldahl flask (as described above) and diluted with 100 cc. of water. Five-tenths g. of aquo salt (containing 0.08 g. of iron) was then added in the solid form and the flask was evacuated with a suction pump until the golden-brown liquid boiled at room temperature. The stopcock was closed and the flask was connected by means of pressure tubing to a gasometer filled with oxygen under a pressure slightly greater than one atmosphere. The stopcock was opened and the flask was shaken with oxygen for  $7^1/2$  hours. At the end of this time the color had changed to dark reddish-brown.

The reaction mixture was poured into a large evaporating dish and after the addition of 2 g. of sodium bicarbonate was evaporated to dryness on a water-bath. During the evaporation the solution became decolorized and ferric hydroxide was formed. The dry residue was dissolved with water, the solution filtered and diluted to 100 cc. A urea determination was made on half of this solution.

The effect of potassium cyanide is discussed on p. 2976. The reactions were carried out by passing oxygen (from a cylinder) through the solutions instead of shaking them with oxygen under pressure.

In Table II the effect of "activated" uracil is shown. Uracil was activated by boiling it for an hour in a Kjeldahl flask (as described above) with about 700 cc. of water and then lowering the required amount of solid aquo salt into the boiling solution by means of a test-tube. After the solution had boiled for 10 minutes longer the ground-glass stopper, with the stopcock open, was fitted into the flask and boiling was continued until steam came out of the open end of the tube. The burner was then removed and the stopcock closed. After cooling to room temperature the contents of the flask and test-tube were mixed by shaking. In Expt. 2 the reaction mixture was allowed to stand for 43 hours after mixing and in Expt. 3, for 24 hours.

# Experiments with Ferrous Sulfate Plus Oxygen or Hydrogen Peroxide

The experiments with ferrous sulfate plus oxygen were carried out in the same manner as those with aquo salt and oxygen under pressure. When hydrogen peroxide was used instead of oxygen, it was added to the solution last and the flask was shaken with the stopcock open.

On evaporation with sodium bicarbonate, the iron was precipitated as ferroferric oxide, Fe₃O₄, instead of ferric hydroxide. Before evaporation with sodium bicarbonate the iron was already precipitated to some extent as a red ferric salt; the solution itself, however, remained colorless.

The writers wish to acknowledge the helpful suggestions and criticisms of Professor Treat B. Johnson during the progress of this work.

17 Chandra, Dissertation, Berlin, 1913.

#### Summary

- 1. The action of ferrous salts on pyrimidines is described under conditions similar to those found in biological processes.
- 2. The reagents used were: (a) FeSO_{4.7}H₂O + NaHCO₃ + air; (b) [Fe(CN)₅OH₂]Na₃ + O₂ or air; (c) FeSO_{4.7}H₂O + O₂; (d) FeSO_{4.7}H₂O + H₂O₂.
- 3. The cleavage may be considered to take place in two steps: (a) partial hydrolysis and oxidation with the formation of intermediate compounds; (b) complete hydrolysis of the intermediate compounds.

The extent of cleavage is determined by a quantitative estimation of the urea formed. In the case of thymine, acetol and pyruvic acid could be identified as reaction products, a fact which confirms the work of Johnson and Baudisch.⁴

- 4. It was shown experimentally that the reactions described are brought about by means of auxiliary valences of the ferrous compounds and pyrimidines. The proof was obtained by: (a) occupation (poisoning) of the auxiliary valences of the iron nucleus by sodium hydroxide, potassium cyanide, ammonia or pyrimidines; this poisoning in most cases was indicated by accompanying color reactions; (b) hydrogenation of the pyrimidine ring; (c) stabilization of the pyrimidine ring by a methyl group in Position 5.
- 5. The relatively greater efficiency of the complex ferrous salt as compared with an ordinary ferrous salt (FeSO_{4.7}H₂O) has been shown.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YAI,E UNIVERSITY]

### THE OXIDATION OF URIC ACID WITH FERROUS SALTS. I

By Mimosa Hortense Pfai,tz Received February 1, 1923

Introduction.—It was desired to determine the behavior of complex iron salts in the presence of oxygen toward uric acid, the most important member of the purine group. Like the pyrimidines, this compound is of great biological significance, being a product of nuclear metabolism, as well as being further oxidized in the animal body. This oxidation, whatever its nature, takes place under mild conditions (weak alkali and body temperature) and if uric acid could be oxidized in the laboratory under similar conditions, the identification of the products of oxidation might throw some light on the mechanism of uric acid metabolism. With this idea in mind the present investigations were undertaken.

As it has already been shown that pyrimidines can be broken down in the presence of these same complex salts, these investigations were carried out in a manner analogous to those on the pyrimidines.

¹ Pfaltz and Baudisch, This Journal, 45, 2972 (1923).

The Action of Ferrous Sulfate Plus Sodium Bicarbonate Plus Air on Uric Acid.—The system, ferrous sulfate plus sodium bicarbonate plus air, effects a partial decomposition of the purine molecule and it was found as with pyrimidines¹ that it is necessary to heat the oxidized solution on the water-bath before the formation of urea takes place. To a solution of 0.5 g. uric acid in 1000 cc. of water containing 36 g. of sodium bicarbonate (12 molecular equivalents) was added 10 g. of ferrous sulfate and the reaction mixture shaken until the ferrous carbonate peroxide was oxidized to ferric hydroxide. A determination of urea directly after oxidation gave no trace of urea, but after the heating on the water-bath, 29% of urea was formed.

The Action of Sodium Pentacyano-aquo-ferroate Plus Oxygen or Air on Uric Acid.—The experiments for determining the action of the system sodium pentacyano-aquo-ferroate plus oxygen or air were carried out in exactly the same way as those with pyrimidines, with the exception that the uric acid was added to the oxidation mixture as a solid instead of as a solution. As the oxidation proceeds the solution of aquo salt gradually turns red, thereby indicating that a loose combination is formed between the auto-oxidizing agent and the uric acid. This shows that an activation of uric acid takes place, and as it has been shown already that activated oxygen is present in a solution of aquo salt, it is safe to assume here also, that the oxidation is brought about by the interaction of activated oxygen and activated uric acid.

At the same time it was observed that the ammine salt brings about a greater cleavage of uric acid than the aquo salt when both are used under the same conditions. The reason undoubtedly is that the liberated ammonia reacts with the suspended uric acid to form an ammonium salt of uric acid, thereby increasing the concentration of uric acid in solution, thus accelerating the oxidation. These results are indicated by the fact that when 0.100 g. of uric acid and 0.30 g. of auto-oxidizing agent were used, and the solutions oxidized by means of a stream of oxygen for 21 hours, the aquo salt gave a break of 57.7% and an ammine salt of 60.6%.

Very little speculation can be made concerning the mechanism of the reaction between the aquo or ammine salt and uric acid, except the supposition that again an intermediate product is formed before cleavage to urea takes place. However, this intermediate compound is considerably more unstable than the corresponding intermediate product formed when uracil or thymine are oxidized. This is shown by the fact that evaporation of the neutral oxidized mixture brings already a cleavage with a yield of about 50% of urea, while heating after the addition of sodium hydrogen carbonate brings about a yield of urea which is in the neighborhood of 75%.

When 0.100 g. of uric acid and 0.30 g. of aquo salt were subjected to a

² Baudisch, Ber., 54, 413 (1921).

stream of oxygen for 86 hours, direct evaporation of the water gave 46.9% of urea and evaporation in presence of sodium bicarbonate gave 71.5% of urea.

The great susceptibility of the uric acid molecule to the influence of the aquo and ammine salts is shown in two ways. First, uric acid can be extensively oxidized by atmospheric oxygen alone, provided the aquo or ammine salts are used as the auto-oxidizing agents and second, the large yields of urea obtained indicate that the uric acid molecule was more completely decomposed than was the case with the pyrimidines. However, the exact role of the ammine and aquo salt is not known, since the yields of urea are in no way proportional to the amount of salt used.

When 0.75 molecular equivalent of aquo salt is used per equivalent of uric acid (namely 0.30 g. of aquo salt per 0.10 g. of uric acid) all of the uric acid ultimately goes into solution during oxidation, and a yield of approximately 75% of urea is obtained. By increasing the relative amount of auto-oxidizing agent, or by increasing the time of oxidation, it was hoped that the yields of urea could be increased. However, by neither of these means was this possible; in fact, it was observed that a great excess of aquo salt tends to decrease the yield of urea.

In each experiment 0.100 g. of uric acid and 200 cc. of water were used and the solutions oxidized by shaking with oxygen under pressure.

#### TABLE I

	Percentage Decomposition with	Different	Amounts	of Aguo	SALT
	Aquo salt, g	0.30	0.40	0.50	1.00
	Time of oxidation	23 h.	48 h.	7.5 h.	44.5 h.
•	Urea formed, %	73.3	75.9	75.1	53.3

These results indicate that the reaction may be catalytic in nature. In this case very much smaller amounts of aquo salt should bring about a relatively large cleavage of uric acid, and this is indeed found to be the case. When amounts of aquo salt are used which correspond to  $^{1}/_{4}$  and  $^{1}/_{40}$  the amount necessary for a reaction taking place molecule per molecule, values of urea are obtained which are much greater than can result from a reaction taking place in equimolecular proportions. In fact, no stoichiometric relationship whatsoever can be seen between the amounts of aquo salt used and the urea formed.

Nevertheless, all of the uric acid cannot be brought into solution by these small amounts of aquo salt, and thus the completion of reaction is still dependent to some extent on the amounts of auto-oxidizing agent used.

These results find no analogy in the behavior of pyrimidines. For instance, if uracil is oxidized with amounts of aquo salt which correspond to  $^1/_6$  and  $^1/_{60}$  the amount necessary for a reaction taking place in equimolecular proportions, the respective amounts of urea obtained are considerably less than  $^1/_6$  and  $^1/_{60}$  of the calculated yield.

#### TABLE II

Comparison of Oxidation of Uric Acid and Uracil with Small Quantities of Aquo Salt

In each experiment 0.200 g. of uracil or 0.100 g. of uric acid and 200 cc. of water were used and the solutions oxidized by shaking with oxygen under pressure for 21.5 hours.

	1	2	3	4
Material used	0.2 g. uracil	0.2 g. uracil	0.1 g. uric acid	0.1 g. uric acid
Amt. of aquo salt, g	0.10	0.01	0.10	0.01
Frac. of cale. amt		1/60	1/4	1/40
Urea formed, %	6.4	0.28	47.3	16.7

The behavior of uric acid and aquo salt indicates the possibility that we are dealing with a case of true catalysis, that is, a molecule of aquo salt is able to function more than once in the activation of oxygen and uric acid. Ultimately, however, the delicate aquo salt molecule must break down under the strong oxidizing influence of pure oxygen under pressure, thus preventing its catalytic effect from continuing.

The Action of the System, Ferrous Sulfate Plus Oxygen.—It was found that the system, ferrous sulfate plus oxygen, is not able to bring about a cleavage of the uric acid molecule.

#### Experimental Part

Apparatus.—The same types of apparatus were used as have been previously described.¹

Analytical Methods.—The urea was determined quantitatively by the method of Fosse³ using the precautions mentioned in a preceding article.¹ Calculations are based on the assumption that each molecule of uric acid can break down to form two molecules of urea.

Experiments with Ferrous Carbonate Peroxide.—The uric acid was dissolved in aqueous sodium bicarbonate solution, to which was then added solid ferrous sulfate. No attempts were made to precipitate the ferrous carbonate in the absence of air. Urea determinations were made on aliquot portions of the clear solution.

Experiments with Sodium Pentacyano-aquo-ferroate.—A weighed portion of uric acid was added to an aqueous solution of the complex salt and the resulting suspension oxidized either by a stream of oxygen or by oxygen under a pressure slightly greater than one atmosphere. When oxidation was discontinued the suspended uric acid had always completely dissolved with the exception of Expts. 3 and 4, Table II.

Experiments with Ferrous Sulfate Plus Oxygen.—A weighed amount of uric acid was added to an aqueous solution of ferrous sulfate containing two molecular equivalents of ferrous sulfate per equivalent of uric acid. Oxidation was attempted by using oxygen under a pressure slightly greater than one atmosphere.

³ Fosse, Ann. chim., [9] 6, 13 (1916).

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# Summary

- 1. The mild conditions under which uric acid is oxidized are emphasized.
- 2. The extent of cleavage of uric acid by means of complex iron salts is shown.
- 3. No mechanism is suggested, but it is demonstrated that an intermediate compound must be formed because the very sensitive xanthydrol test is obtained only after the oxidation mixture has been heated on the water-bath.
- 4. Experiments show that the oxidation of uric acid by means of [Fe(CN)₅H₂O]Na₃ may be catalytic in nature, and brought about by means of auxiliary valences. The latter is proved by the formation of a brilliant red solution during oxidation.

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# CONDENSATIONS OF ALDEHYDES WITH RESORCINOL AND SOME OTHER AROMATIC HYDROXY COMPOUNDS

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The condensation of aldehydes with various aromatic hydroxy compounds has been previously studied by several investigators. A close study of these condensations brings out certain facts of great importance, as follows.

- 1. Though the modes in which these various condensations took place and the natures of the resulting products were different in many cases, yet in a few cases only two molecules of hydroxy compounds reacted with one molecule of the aldehyde, forming the pyrone ring with the elimination of water by the interaction of two hydroxyl groups in the *ortho* position to the reacting hydrogen atoms. The mode in which these condensations were carried out by the previous workers may be generally represented either as Type 1^{1f} or Type 2^{1e} (R is a phenyl residue).
- (a) Michael, Am. Chem. J., 5, 339 (1883).
   (b) Causse, Bull. soc. chim., [3] 3, 861 (1890).
   (c) Hewitt and Pope, Ber., 29, 2824 (1896).
   (d) Michael, J. prakt. Chem., 165, 334 (1898).
   (e) Weidel and Wenzel, Monatsh., 21, 61 (1900).
   (f) Pope and Howard, J. Chem. Soc., 78, 1023 (1910).
   (g) Michael and Comey, Am. Chem. J., 5, 349 (1883).
   (h) Liebermann and Lindenbaum, Ber., 37, 2728 (1904).
   (i) Fischer and Jennings, Ber., 27, 1355 (1894).
   (j) Hofmann, Ber., 26, 1139 (1893).
   (k) Zenoni, Gazz. chim. ital., 23, II, 215 (1893).
   (e) Trzcinski, Ber., 17, 499 (1884).
   (m) Möhlau and Koch, Ber., 27, 2887 (1894).

2. Even in those few cases where such pyrone-ring formation took place, the xanthenes were first isolated and then oxidized by different oxidizing agents to the corresponding fluorones. For instance, in Möhlau and Koch's work^{1m} formaldehyde was first condensed with resorcinol by means of dil. sulfuric acid to form the xanthene; this xanthene was then isolated and in turn oxidized to fluorone by heating with concd. sulfuric acid, the reactions being represented thus,

HO OH HO OH dilute 
$$H_2SO_4$$
 HO OH HO OH  $H_2SO_4$   $H_1$   $H_2SO_4$   $H_1$   $H_2SO_4$   $H_1$   $H_2SO_4$   $H_1$   $H_2SO_4$   $H_1$   $H_2SO_4$   $H_1$   $H_1$ 

3. The condensing agents used in the previous work were alcohol, sodium hydroxide, moderately concd. sulfuric acid, or alcoholic sulfuric acid, which could not bring about pyrone-ring formation and oxidation in one stage.

The present investigation has been taken up with two objects in view. The first is to study whether any such pyrone ring giving rise to xanthene can be formed and whether such leuco compounds can be oxidized to the corresponding fluorones in one stage by using the same condensing agent, thereby opening up new possibilities of the preparation of benzeins.

The second object has its origin in the fact that the majority of the compounds prepared during the course of this investigation are fluorescent, the fluorescence depending on the nature and position of certain groups.

It is therefore of considerable interest to study the influence of the number and position of hydroxyl and carboxyl groups on the existence and intensity of fluoresence, and also the influence of temperature and nature of the solvent.

Attention was first directed to find out a suitable condensing agent for bringing about the desired condensation as indicated before. With this object in view, sulfuric acid, d. 1.750, was first used as the condensing agent, but with this acid a product was obtained at 100° the alkaline solution of which was not fluorescent, which was insoluble in cold water and had no dyeing property, that is, it did not exhibit the characteristic properties of a benzein. Consequently, the temperature was raised to 200°, but at that high temperature ofly tarry product was obtained.

Next, acid of d. 1.840 was used and the condensation was effected by heating the reacting substances on the water-bath for about an hour; sulfur dioxide was evolved. It was found by testing the product that the desired result was obtained, that is, the product was insoluble in cold water, the alkaline solution was fluorescent and it possessed all the characteristic properties of a benzein.

Most of the compounds described in this paper have been obtained by condensing aldehydes with some aromatic hydroxy compounds by using the same condensing agent.

In order to study whether the reaction is of general application, different aldehydes have been used such as (1) chloral hydrate and paraldehyde from the aliphatic series, (2) benzaldehyde and substituted benzaldehydes from the aromatic series, (3) furfurole from the heterocyclic group and (4) phenetole-azo-benzaldehyde-sulfonic acid, which is a complex aldehydic compound with an azo group.

The mechanism of the reaction is explained as follows. The reaction takes place in several stages: (1) the two hydrogen atoms of the hydroxy compound in *ortho* position to one hydroxyl group and in *para* position to the other, interact with aldehydic oxygen; (2) then the two hydroxyl groups interact with the elimination of one molecule of water, giving rise to xanthenes; (3) these in turn are oxidized to fluorones at the expense of sulfuric acid, as is evident by the evolution of sulfur dioxide, the formation of which was indicated by development of a blue color on starch-iodide paper and the odor; (4) these oxidized products then assume the quinonoid structure by the elimination of another molecule of water. These various steps are indicated on the next page.

This constitution as given in the case of resorcinol-benzein is supported by the following facts: (1) analytical results show that its molecular formula is  $C_{19}H_{12}O_3$ ; (2) analysis shows the formation of a monopotassium salt, and therefore indicates the presence of only one hydroxyl group; (3) analysis shows the formation of a monobenzoyl derivative, indicating

thereby the presence of one hydroxyl group; (4) the physical properties, such as fluorescence, intensity of color, affinity for wool and silk, etc., are also in agreement with the suggested constitution.

Most of the compounds prepared during the course of this investigation dye wool and silk from an acid bath in yellow, orange or brown shades depending on the number, position and nature of the substituting groups, bromo compounds producing red and bluish-red shades. This may be illustrated by the following examples.

Dye	Shade of original compound	Shade of bromo compound	Remarks
1. Resorcinol- benzein	Yellow	Red	
2. Resorcinol- hydroxy- benzein	More orange than 1	Deeper than 1	Influence of one more OH group
3. Resorcinol- dihydroxy- benzein	More orange than 1	More bluish than 1	Influence of two OH groups
4. Resorcinol- phenetole- azo-benzein- sulfonic acid	Brown	More bluish than 1	Influence of additional azo group

These compounds resemble the fluoresceins in constitution and properties. Taking resorcinol-benzein as the typical compound of this series and fluorescein to be the typical compound of the fluoresceins, a comparison of their properties is of interest. Both compounds are precipitated from their solutions in sodium hydroxide as yellowish-red powders; both dissolve in alcohol with yellow-red color and green fluorescence, the intensity of which is greater in the case of fluorescein; both dissolve in sodium hydroxide giving dark red concd. solutions, but on dilution fluorescein gives an orange-green fluorescence and resorcinol-benzein gives a red-green fluorescence fluorescence.

orescence; both compounds can be brominated to tetrabromo compounds which dye wool and silk beautiful red shades. One very interesting fact about these compounds is that resorcinol-benzein is quinonoid in all its tautomeric forms,

while fluorescein is not quinonoid in all its tautomeric forms.

According to Watson's rule² a dye which is quinonoid in all its tautomeric forms should produce a deep shade (violet, blue or green). Resorcinol-benzein is, however, not of such a deep color, although it produces a deeper, more orange shade than fluorescein.

The second object of the present investigation is to study (1) the influence of the number and positions of hydroxyl and carboxyl groups, and (2) the influence of the temperature and the nature of the solvent on the existence and the intensity of fluorescence of these compounds.

Taking fluorescein to be the typical fluorescent substance, a comparison between this compound and other compounds with different groups in different positions is interesting.

Resorcinol-benzein (I) (or the sodium salt) which differs from fluorescein (II) by the absence of one carboxyl group in the phenyl residue in *ortho* ² Watson, J. Chem. Soc., 105, 759 (1914).

position to the central methane carbon atom is less fluorescent than fluorescein. That the intensity of fluorescence of these compounds is much less than that of the fluoresceins appears to be due to the fact that the intermediate phase is not strictly symmetrical.³

To study the effect of an hydroxyl group in *ortho* and *para* positions to the central methane carbon atom, resorcinol-o-hydroxybenzein and resorcinol-p-hydroxybenzein have been prepared. Both compounds are fluorescent in sodium hydroxide solution, the *ortho* compound showing a bluish fluorescence and the *para* compound exhibiting a greenish fluorescence of slightly greater intensity.

The effect of an additional methoxy group in the *meta* position to the central methane carbon atom is not very marked as shown by resorcinol-p-hydroxy-m-methoxybenzein, whereas resorcinol-p-methoxybenzein exhibiting bluish fluorescence shows the effect of a methoxy group in the para position, resorcinol-benzein as well as resorcinol-p-hydroxybenzein exhibiting green fluorescence.

Resorcinol-*m*-carboxy-*p*-hydroxybenzein, the condensation product of 5-aldehydo-salicylic acid and resorcinol, showed the influence of the carboxyl group in the *meta* position to the central methane carbon atom. This compound is feebly fluorescent. It has been shown that the presence of an hydroxyl group in the *para* position to the central carbon atom produces fluorescence. Now, as this compound, which contains one hydroxyl group in the *para* position and one carboxyl group in the *meta* position to the central carbon atom, is feebly fluorescent, it is logical to conclude that its feebly fluorescent character is due to the presence of the carboxyl group in the *meta* position. Here it is interesting to note the marked effect on fluorescence of a carboxyl group when in different positions in the phenyl residue.

 $\beta$ -Resorcylic-acid-benzein and gallic-acid-benzein show the influence of substituents in the benzene nuclei associated with pyrone oxygen. The former, having one carboxyl group in Position 2 and another in Position 7, is fluorescent while the latter, having one carboxyl group in Position 1 and another in Position 8, is not. Non-fluorescence of the latter in sodium hydroxide is due to (1) the presence of hydroxyl groups in the 4 and 5 positions and (2) the unsymmetrical intermediate phase,

³ Hewitt's Theory of Double Symmetrical Tautomerism, *Proc. Chem. Soc.*, 16, 3 (1900).

One interesting fact about gallic-acid-benzein is that it is not fluorescent in alkaline solution, while its solution in coned. sulfuric acid is fluorescent. Instances of this type are already known; fluoran, for example, fluoresces in coned. sulfuric acid solution but not in alcoholic solution.

In pyrogallic-acid-benzein there are two hydroxyl groups in Positions 4 and 5, and also one in 6. This substance is not fluorescent. Its non-fluorescent character is most probably due to the presence of hydroxyl groups occupying positions *ortho* to pyrone oxygen, that is, the 4 and 5 positions. Such instances are also known in the case of fluorane derivatives.

Resorcinol-ethein, having a methyl group in place of the phenyl residue, is also fluorescent. Resorcinol-phenetole-azo-benzein-sulfonic acid is not fluorescent. This may be due to the presence of azo and sulfonic acid groups.

It is a curious fact that tetrabromo compounds of resorcinol-benzein, resorcinol-o-hydroxy-benzein, resorcinol-p-methoxy-benzein are non-fluorescent in sodium hydroxide, pyridine, and sulfuric acid solutions but are fluorescent in alcoholic solution, this fluorescence disappearing on dilution.

The effect of the influence of temperature on the intensity of fluorescence has been noted in a few cases. The fluorescence of certain substances, such as resorcinol-benzein, disappears at a higher temperature but reappears on cooling. This phenomenon has not yet received any satisfactory explanation. It may be due to the change of velocity of electrons and the consequent change in the period of vibration.

To study the influence of the nature of the solvent on the intensity and existence of fluorescence the following solvents were used: dil. aqueous sodium hydroxide, concd. sulfuric acid, redistilled ethyl alcohol, ether, glacial acetic acid, benzene, nitrobenzene, pyridine, acetone and in some cases methyl alcohol. From the observations recorded in the experimental part it may be concluded that the majority of compounds are fluorescent in sodium hydroxide and alcoholic solutions, and a few in pyridine and in sulfuric acid solutions. The majority of the substances, being insoluble in glacial acetic acid, benzene and ether, do not exhibit fluorescence in these liquids.

In consideration of the fact that the relation between chemical constitution and fluorescence has been very little investigated the results obtained during the course of this work have considerable theoretical interest.

# Experimental Part

1. Resorcinol-benzein  $C_{19}H_{12}O_3$  (I).—To a solution of 4.6 g, of dried resorcinol in 5 cc. of warm concd. sulfuric acid (d., 1.840) in a 300cc. conical flask fitted with an air condenser was added 2.2 cc. of dry benzaldehyde drop by drop and the mixture stirred constantly. Great heat was generated and an intense yellow color developed in the course of two or three minutes. When all of the benzaldehyde had been added, the flask with the contents was heated on the water-bath for about 45 minutes, when the odor of benzaldehyde was no longer perceptible. During the course of heating sulfur dioxide was evolved, as was evidenced by its odor and by the development of a blue color on starch-iodide paper.

When the mass became solid it was cooled, treated with ice-cold water, filtered and washed with cold water. The precipitate was dissolved in a solution of sodium hydroxide which was filtered and the original compound was reprecipitated with dil. hydrochloric acid, after which solution and precipitation were repeated. The product was finally crystallized from ethyl alcohol, when a microcrystalline yellow powder was obtained, and dried at 100°; yield, 3.8 g., or 74%. It is insoluble in cold water, ether, benzene, or glacial acetic acid, and is soluble in hot water (giving a yellow solution), in sodium hydroxide (a red solution), in coned. sulfuric acid (an orange solution), in acetone (a yellow solution), and in alcohol (a reddish-yellow solution). It imparts a redgreen fluorescence to sodium hydroxide solution and pyridine solution, and an orange-green fluorescence to sulfuric acid and alcoholic solutions. Its solution in sodium hydroxide becomes colorless when heated with zinc dust, and again becomes colored by oxidation on exposure to air. It does not melt below 290°. On heating the substance on a nickel spatula over the flame it decomposes without melting. It dyes wool and silk a yellow shade.

Analyses. Subs., 0.1520, 0.1600: CO₂, 0.4402, 0.4640;  $H_2O$ , 0.0564, 0.0593. Calc. for  $C_{19}H_{12}O_3$ : C, 79.16; H, 4.16. Found: C, 78.98, 79.09; H, 4.12, 4.11.

Potassium Salt.—Four g. of purified resorcinol-benzein was just neutralized with potassium hydroxide solution. The resulting salt solution was then filtered, the filtrate evaporated to a small bulk, and the neutral monopotassium salt was precipitated by alcohol. It was filtered off and finally crystallized from hot dil. alcohol as red crystals, which dissolve in water to give a red solution with red-green fluorescence.

Analysis. Subs., 0.1300:  $K_2SO_4$ , 0.0344. Calc. for  $C_{19}H_{11}O_3K$ : K, 11.99. Found: 11.8.

The Benzoate.—Five g. of pure resorcinol-benzein was benzoylated by the Schotten-Baumann process. There was thus obtained a light yellow powder which was purified by crystallization from alcohol. It melted at 141–142°.

Analyses. Subs., 0.1500, 0.1520:  $CO_2$ , 0.4373, 0.4430;  $H_2O$ , 0.0550, 0.0560. Calc. for  $C_{26}H_{16}O_4$ : C, 79.59; H, 4.08. Found: C, 79.44, 79.48; H, 4.07, 4.06.

2,3,5,7-Tetrabromo Derivative.—Five g. of the compound was brominated in alcohol by the slow addition of the calculated amount of liquid bromine. The product was crystallized from alcohol and was obtained as a red microcrystalline powder. It is soluble in sodium hydroxide solution (orange color, no fluorescence), in alcohol (orange color, feeble orange-green fluorescence), and insoluble in benzene or acetone. It dyes wool and silk a reddish-orange shade from an acid bath. It decomposes at about 200°.

Analysis. Subs., 0.1500: AgBr, 0.1866. Calc. for C₁₉H₈O₅Br₄: Br, 52.98. Found (Piria and Schiff's method): 52.93.

Resorcinol-benzein has been prepared previously by two other methods: (1) benzo-trichloride was condensed with resorcinol by heating the mixture on the paraffin-bath at 180° to 190° for five or six hours with zinc chloride; (2) benzoic acid was similarly condensed with resorcinol. The present method is simpler and more advantageous than the previous ones, as in this method less time and less energy (reaction temperature being the temperature of the water-bath) are required. The difficulty of the preparation of resorcinol-benzein by the earlier methods probably accounts for the fact that this substance did not gain so much importance as fluorescein.

2. Resorcinol-1'-hydroxybenzein.—A mixture of 4.6 g. of dried resorcinol, 2.4 cc. of salicylic aldehyde and 10 cc. of concd. sulfuric acid was heated on an oil-bath to 110° for 1¹/₂ hours. The product was then treated and purified in the same manner as described in the case of resorcinol-benzein. It is soluble in sodium hydroxide solution (orange color, red-blue fluorescence), in alcohol (yellowish-red color, no fluorescence), in

acetone (yellow color, no fluorescence), in nitrobenzene (yellow color, no fluorescence) or in pyridine (deep red color, dull green fluorescence), and is insoluble in glacial acetic acid, benzene or ether. It does not melt below 260°. It dyes wool and silk a yellow-ish-orange shade from an acid bath.

Analyses. Subs., 0.1450, 0.1420:  $CO_2$ , 0.3982, 0.3886;  $H_2O$ , 0.0508, 0.0508. Calc. for  $C_{19}H_{12}O_4$ : C, 75.00; H, 3.94. Found: C, 74.89, 74.63; H, 3.80, 3.98.

Tetrabromo Derivative.—Five g. of the substance was brominated by the slow addition of liquid bromine (1.5 cc.) to the alcoholic solution. The bromo compound was crystallized from alcohol and was obtained as red crystals; yield, 5.6 g. It is soluble in sodium hydroxide (red color, no fluorescence), in alcohol (orange-yellow color, feeble yellowish-green fluorescence), in coned. sulfuric acid (yellow solution, no fluorescence) or in pyridine (orange solution, no fluorescence). It decomposes at about 210° with change of color. It dyes wool and silk a red shade.

Analysis. Subs., 0.1512: AgBr, 0.1830. Calc. for  $C_{10}H_8O_4Br_4$ : Br, 51.58. Found: 51.52.

3. Resorcinol-2'-methoxy-3'-hydroxybenzein (III).—An intimate mixture of 6.6 g. of dried resorcinol with 4.6 g. of dried vanillin was added little by little to 10 cc. of coned. sulfuric acid (d., 1.840) in a conical flask with an air condenser, and the flask was heated on the oil-bath at 110–115° for about an hour. The subsequent process of purification was the same as in the case of the resorcinol-benzein. When crystallized from ethyl alcohol it formed a grayish-black, microcrystalline powder; yield, 5 g. It dissolves in sodium hydroxide solution (reddish-violet color, green fluorescence) and in coned. sulfuric acid (pink color, green fluorescence). It is insoluble in ether or benzene. It forms a bromo compound on treatment with liquid bromine, and dyes wool and silk from an acid bath with a yellowish-orange shade. It does not melt below 295°.

Analyses. Subs., 0.1600, 0.1301:  $CO_2$ , 0.4200, 0.3446;  $H_2O$ , 0.0599, 0.0487. Calc. for  $C_{20}H_{14}O_5$ : C, 71.80; H, 4.15. Found: C, 71.59; 71.74; H, 4.16, 4.17.

4. Gallic-acid-benzein (IV).—Six and eight-tenths g. of well-dried gallic acid was condensed with 2.1 cc. of dried benzaldehyde in the same manner as in the case of the resorcinol-benzein, except that in this case the reacting substances were heated on an oilbath to 120–125° for two hours. The substance was dissolved in sodium hydroxide and was reprecipitated by addition of dil. hydrochloric acid. It was then dissolved in 75% alcohol and the alcoholic solution was poured into hot water, when a precipitate was formed. The precipitate was again crystallized from hot alcohol, and a greenish microcrystalline powder was obtained; yield, 4 g. It dissolves in sodium hydroxide (deep red color, no fluorescence, and in coned. sulfuric acid (brownish-red color, red-green fluorescence). That the substance does not undergo any change in the sulfuric acid solution is proved by the fact that when the sulfuric acid solution is diluted with water the original substance is reprecipitated. It dissolves in acetone (yellowish-green color, no fluorescence), in alcohol (greenish color, no fluorescence), in pyridine (yellow color, no fluorescence), in alcohol (greenish color, no fluorescence), in pyridine (yellow color, no fluorescence)

cence), and in nitrobenzene (greenish solution); it is insoluble in glacial acetic acid in the cold but dissolves slightly when heated, and is insoluble in benzene and ether. It is a mordant dye, giving a brown shade in chrome-mordanted wool. It softens at 198°.

Analyses. Subs., 0.1300, 0.1640:  $CO_2$ , 0.2941, 0.3712;  $H_2O$ , 0.0345, 0.0439. Calc. for  $C_{21}H_{12}O_9$ : C, 61.76; H, 2.94. Found: C, 61.69, 61.73; H, 2.95, 2.97.

5. Condensation of Chloral Hydrate and Resorcinol (V).-To the solution of dried resorcinol in sulfuric acid was added 4.95 g. of dried chloral hydrate. The first action of sulfuric acid was to liberate the aldehyde chloral which acts on resorcinol. The reaction mixture was heated on the water-bath, when there was much frothing and copious fumes of hydrogen chloride (detected by the formation of ammonium chloride) and sulfur dioxide (detected by starch-iodide paper) escaped. The heating was continued for four to five hours. The cold mass was treated with ice-cold water. As the substance is soluble in cold water, the least quantity of water, containing a little hydrochloric acid, was used in washing. The same method of purification was adopted as in the case of the first compound; yield, 2 g. It dissolves in sodium hydroxide solution (red color, red-green fluorescence) and in sulfuric acid (yellow color, no fluorescence). One peculiarity of this substance is that the red color of the alkaline solution changes to orange on dilution. It is insoluble in glacial acetic acid, benzene, ether or acetone. The substance did not give any test for halogen. It dissolves in sodium carbonate solution with evolution of carbon dioxide. It dyes wool and silk a very light yellow. It does not melt below 295°.

Analyses. Subs., 0.1400, 0.1200: CO₂, 0.3362, 0.2877; H₂O, 0.0390, 0.0335. Calc. for C₁₄H₈O₅: C, 65.62; H, 3.12. Found: C, 65.49, 65.38; H, 3.09, 3.10.

6. Resorcinol-ethein (VI).—Four and four-tenths g. of dried resorcinol was condensed with 1.76 cc. of paraldehyde in the usual manner. Ice-cold water was poured into the solid mass, the precipitate thus formed was dissolved in sodium hydroxide solution, the compound reprecipitated by dil. hydrochloric acid, the solution filtered, and the substance dried, washed with benzene and finally crystallized from 75% alcohol. It was obtained as a black, microcrystalline powder. It does not melt or decompose below 290°. It dissolves in sodium hydroxide solution (red color, red-green fluorescence, the intensity of which is almost equal to that of resorcinol-benzein). It is soluble in alcohol (orange color) and is insoluble in ether, benzene or nitrobenzene. It dyes wool and silk a yellowish-orange shade.

Analyses. Subs., 0.1200, 0.1350:  $CO_2$ , 0.3264, 0.3665;  $H_2O$ , 0.0476, 0.0534. Calc. for  $C_{14}H_{19}O_3$ : C, 74.34; H, 4.40. Found: C, 74.18, 74.04; H, 4.40, 4.39.

7. Resorcinol-phenetole-azo-benzein-sulfonic Acid (VII).—A thorough mixture of 6.8 g. of recrystallized azo-aldehyde⁴ with 4.4 g. of resorcinol in a mortar was added, little

⁴ Green and Sen, J. Chem. Soc., 97, 2243 (1910).

by little, to 10 cc. of sulfuric acid. A deep red color developed and great heat was generated. The mixture was thoroughly stirred and heated on an oil-bath at 130–140° for three hours. Sulfur dioxide was evolved. The solid mass was treated with ice-cold water. A portion was tested to prove the absence of azo-aldehyde, by means of phenylhydrazine acetate. The usual method of purification was followed; yield, 3 g. It dissolves in sodium hydroxide solution (brown color), in alcohol (brownish-yellow color) and in sulfuric acid (brown-red color). It is insoluble in nitrobenzene or ether. It does not fluoresce in any of the solvents, perhaps owing to the presence of sulfonic acid and azo groups. It dyes wool and silk from an acid bath a brownish-yellow shade.

Analyses. Subs., 0.1679: 8.5 cc. of  $N_2$  (30°, 760 mm.). Calc. for  $C_{27}H_{20}O_7N_2S$ : N, 5.5; S, 6.20. Found: N, 5.50; S, 6.00.

8. Resorcinol-furfurein (VIII).—To a solution of 6.6 g. of resorcinol in 10 cc. of sulfuric acid in a flask surrounded by freezing mixture was added 2.6 cc. of furfurole drop by drop while the mixture was constantly stirred. The substance assumed first a blue, then a reddish-violet and finally a blue-black color. After all of the furfurole had been added the flask was heated on the water-bath for half an hour, when sulfur dioxide was evolved. The substance is highly soluble in water. Therefore sulfuric acid was removed as barium sulfate by the addition of barium carbonate. The solution was filtered, the filtrate was evaporated to a small bulk and coned. hydrochloric acid was added. The solution was filtered and the precipitate was collected and finally crystallized from alcohol; yield, 3 g. It is soluble in sodium hydroxide solution (red color, red-green fluorescence), in coned. sulfuric acid (reddish-yellow color) and is insoluble in benzene or ether. It does not melt below 280°.

Analyses. Subs., 0.1200, 0.1110:  $CO_2$ , 0.3225, 0.2985;  $H_2O$ , 0.0394, 0.0361. Calc. for  $C_{17}H_{19}O_4$ : C, 73.40; H, 3.60. Found: C, 73.30, 73.34;  $H_2O$ , 3.65, 3.61.

9. Resorcinol-p-hydroxy-m-carboxybenzein (IX).—A mixture of 5 g. of the 5-aldehydo-salicylic acid (prepared by Cohen's modification of Reimer and Tieman's method⁵) with 8.8 g. of resorcinol was added to 20 cc. of sulfuric acid in a conical flask while it was constantly stirred. The mixture was heated on the water-bath for about an hour. At the end of the reaction the product was treated with ice-cold water, purified in the usual manner and obtained as a yellow powder; yield, 3 g. It dissolves in sodium hydroxide solution (red color, red-green fluorescence), in sulfuric acid (yellow color, no fluorescence), in alcohol (yellow color, no fluorescence) and in pyridine (reddish-yellow color, no fluorescence), and is insoluble in nitrobenzene, ether or benzene. It dyes wool and silk a bright yellow shade. It does not melt below 295°.

Analyses. Subs., 0.1300, 0.1350:  $CO_2$ , 0.3241, 0.3385;  $H_2O$ , 0.0409, 0.0428. Cale for  $C_{20}H_{12}O_6$ : C, 68.96; H, 3.44. Found: C, 67.99, 68.38; H, 3.49, 3.52.

10.  $\beta$ -Resorcylic-acid-benzein (X).—Five and six-tenths g. of  $\beta$ -resorcylic acid was condensed with 2.2 cc. of benzaldehyde in the same manner as in the case of re-

⁵ Wayne and Cohen, J. Chem. Soc., 121, 1022 (1922).

sorcinol-benzein. The usual method of purification was adopted, giving a yellow powder; yield, 2.5 g. It is soluble in sodium hydroxide solution (orange color, green fluorescence), in sulfuric acid (yellow color, no fluorescence) and in alcohol (orange-yellow color, no fluorescence).

Analyses. Subs., 0.1200, 0.1220:  $CO_2$ , 0.2944, 0.2997;  $H_2O$ , 0.0346, 0.0343. Calc. for  $C_{21}H_{12}O_7$ : C, 67.02; H, 3.19. Found: C, 66.91, 66.99; H, 3.20, 3.12.

11. Resorcinol-3-methoxybenzein.—A mixture of 4.4 g. of resorcinol, 2.5 cc. of anisaldehyde and 10 cc. of sulfuric acid was heated to 110–115° on an oil-bath for about an hour. The usual method of purification was adopted and the substance was obtained as a yellow powder. It does not melt or decompose below 285°. It dissolves in sodium hydroxide solution (red color, bluish fluorescence), in alcohol (yellow color, no fluorescence), in sulfuric acid (dark red color, no fluorescence) and in pyridine (light yellow color, no fluorescence), and is insoluble in ether or benzene. It dyes wool and silk from an acid bath a bright yellow shade.

Analyses. Subs., 0.1220, 0.1200:  $CO_2$ , 0.3367, 0.3308;  $H_2O$ , 0.0485, 0.0475. Calc. for  $C_{20}H_{14}O_4$ : C, 75.40; H, 4.40. Found: C, 75.27, 75.18; H, 4.41, 4.39.

Tetrabromo Derivative.—Five g. of the pure substance was brominated in the usual manner by the slow addition of 2.5 cc. of liquid bromine. The red precipitate thus obtained was crystallized from alcohol as a red powder. It is soluble in sodium hydroxide solution (deep red color, no fluorescence), in alcohol (reddish-orange color, greenish-orange fluorescence) and in concd. sulfuric acid (reddish-yellow color, no fluorescence). It does not melt, but decomposes at 200°, and dyes wool and silk a red shade.

Analysis. Subs., 0.1200: AgBr, 0.1421. Calc. for  $C_{20}H_{10}O_4Br_4$ : Br, 50.46. Found: 50.30.

12. Pyrogallol-benzein (XI).—A solution of 7.5 g. of pyrogallic acid in 20 cc. of concd. sulfuric acid was condensed with 3.15 cc. of benzaldehyde in the usual manner, and the product, purified as described above, obtained as a brown powder; yield, 2.5 g. It dissolves in sodium hydroxide (yellow solution, no fluorescence), in sulfuric acid (brownish-red solution, no fluorescence), in pyridine (red solution, no fluorescence), in nitrobenzene (red solution, no fluorescence). It does not melt below 295°.

Analyses. Subs., 0.1350, 0.1310:  $CO_2$ , 0.3516, 0.3419;  $H_2O$ , 0.0450, 0.0433. Calc. for  $C_{12}H_{12}O_4$ : C, 71.25; H, 3.75. Found: C, 71.03, 71.17: H, 3.70, 3.67.

# Summary

- 1. Compounds of the type of benzeins have been obtained in good yields by the condensation of various aldehydes with resorcinol and other hydroxy compounds in the presence of concd. sulfuric acid at temperatures varying from 100° to 130°.
- 2. These compounds are more or less fluorescent, the intensity of fluorescence in sodium hydroxide solution varying with the number and the position of hydroxyl and carboxyl groups. Thus, (1) in the phenyl residue R, the ortho position to the central carbon atom is most favorable and the meta position is most unfavorable for the carboxyl group to excite fluorescence; (2a) in the phenyl residue R, the ortho and para positions to the central carbon atom are also favorable for the hydroxyl group, although the effect is not so marked as in the case of carboxyl groups; (2b) in the benzene nuclei associated with the pyrone ring, Position 6 or 3 is

most favorable and 4 and 5 positions are most unfavorable for hydroxyl groups; (3) the influence of hydroxyl groups on fluorescence is greater when they occur in the benzene nuclei than when they occur in the phenyl residue, whereas the influence of carboxyl groups is greater in the phenyl residue than in the benzene nuclei.

3. Bromo derivatives of these compounds which have been studied do not fluoresce in any other ordinary solvents except alcohol.

CALCUTTA, INDIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

#### SOME CACODYL DERIVATIVES

By Frank A. Lee, Curtis Thing and William M. Dehn Received June 9, 1923

#### General

The classical investigations of Robert Bunsen in the cacodyl series have remained substantially free from revision¹ since their publication (1837–1843). This paper develops some new compounds of this series and also concerns itself with reinvestigations of some of Bunsen's compounds, for the purposes both of fixing their formulas and of improving their yields. Though some have been obtained through substitution and oxidation, most of the new compounds herein described are additive or are hydrolytic products of such additive compounds. It is of special interest to note that one chlorine atom of the pentavalent arsenic compounds is characteristically susceptible to hydrolysis.

# **Experimental Part**

Cacodyl was prepared in large quantities by the usual method² and was then converted into cacodyl chloride³ by the use of mercuric chloride. It boiled⁴ at 109°.

Preparation of Cacodyl Bromide. Molecular quantities of potassium bromide and cacodyl chloride with 3 to 4 volumes of absolute alcohol were heated for 4 to 5 hours on a water-bath under a return condenser. Practical exclusion of air is advisable to avoid formation of the hydrated oxybromide. The reaction mixture was distilled from a sand bath as long as any distillate was obtained. The latter was treated with 5 to 10 volumes of water to precipitate the cacodyl bromide, which was then separated, dried with calcium chloride and fractionated. The yield of the bromide, boiling at 130°, was nearly quantitative.

Ostwald's "Klassiker der Exakten Wissenschaften," No. 27, pp. 138-148. Baeyer recalculated some of Bunsen's data with revised atomic weights and proposed some alternate formulas.

² (a) Bunsen, Ann., 37, 6 (1841); (b) 107, 257 (1858). This Journal, 35, 2 (1906).

³ (a) Ref. 2a, p. 30; (b) Ann., 42, 22 (1842).

⁴ Bunsen gave the boiling point as "over 100°."

⁵ Ref. 2a, p. 33. Bunsen prepared this compound in accordance with the reaction,  $[(CH_3)_2As]_2O + 2HgCl_2 + 2HBr \longrightarrow 2(CH_3)_2AsBr + 2HgCl_2 + H_2O.$ 

Cacodyl Iodide.  6 —This was prepared in an analogous manner in nearly quantitative yields. It boiled at 155–160  $^\circ$ .

Cacodyl Cyanide.8—This was prepared from cacodyl chloride and potassium cyanide in an analogous manner. Satisfactory yields of oil boiling at 138° were obtained. Since the cyanide was not found to be excessively poisonous, it probably has the cyanide and not the isocyanide structure. This compound will be studied further.

Cacodyl Chloride and Metallic Sodium.—Equimolecular quantities of the two materials in absolute ether slowly yielded cacodyl and sodium chloride.  $2(CH_3)_2AsCl + 2Na \longrightarrow [(CH_3)_2As]_2 + 2NaCl$ .

Bunsen's "Basic Cacodyl Superchloride."—Cacodyl chloride was found to be oxidized when in contact with moist air, giving rise to odorless, glistening, transparent, prismatic needles. The compound is best prepared by drawing moist air through an ether solution of cacodyl chloride. Dry air gives no crystals.

Analyses. Calc. for (CH₃)₂As(OH)₂Cl: C, 13.75; Cl, 20.32. Found: C, 13.66; Cl, 20.10.

The substance melts at 85°, is soluble in water and alcohol, and is insoluble in ether, chloroform and carbon disulfide. When dissolved in alcohol and reprecipitated by ether it melted at 92° and then contained only 18.00% of chlorine. Bunsen prepared this compound by the action of coned. hydrochloric acid on cacodylic acid: (CH₃)₂AsO.-OH + HCl  $\longrightarrow$  (CH₃)₂As(OH)₂.Cl. Our method of preparation led to the same compound:  $2(\text{CH}_3)_2\text{AsCl} + O_2 + 2\text{H}_2\text{O} \longrightarrow 2(\text{CH}_3)_2\text{As}(\text{OH})_2\text{Cl}$ . A better name for it is hydrated cacodyl oxychloride or simply basic cacodyl chloride.

# Reactions of Cacodyl Chloride with Metallic Chlorides

Mercurous Chloride.—Equimolecular quantities of the two compounds under water slowly yielded a white powdery additive compound. This mixture when boiled yielded cacodyl chloride, mercury, hydrochloric acid and cacodylic acid.  10  (CH₃)₂AsCl + 2 HgCl + 2H₂O  $\longrightarrow$  (CH₃)₂AsO.OH + 3HCl + 2Hg.

Mercuric Chloride.—Equimolecular quantities of the compounds quickly yielded an odorless, white, solid additive compound. When this was heated with water it yielded mercury, mercurous chloride, hydrochloric and cacodylic acids. The hot aqueous filtrate gave odorless glistening white rhombic leaflets, which were decomposed but not melted at 210°.

Analysis. Calc. for (CH₂)₂AsCl(OH)HgCl: Cl, 18.02. Found: 17.98.

Mol. wt. Calc. 393. Found (ebullioscopic method with water): 320.

This compound develops with hydrochloric acid the odor of cacodyl chloride. It is easily decomposed by hot aqueous solutions of alkalies and alkali carbonates. Its formation is explained by the equations,  $(CH_3)_2AsCl + HgCl_2 \longrightarrow (CH_2)_2AsCl_2.HgCl$ ;  $2(CH_3)_2AsCl_2.HgCl + 3H_2O \longrightarrow (CH_3)_2AsCl(OH)HgCl + (CH_3)_2AsO_2H + 3HCl + HgCl$ . Obviously the substance is an additive compound of mercuric chloride and

⁶ Ref. 2a, p. 32. Prepared by Bunsen like the bromide.

⁷ Ann., 92, 364 (1854).

⁸ Ref. 2a, p. 23. Bunsen distilled mixtures of cacodyl and mercuric cyanide and obtained a very poisonous product melting at 33° and boiling at 140°.

⁹ Bunsen's "hydrated cacodyl chloride," (CH₃)₂As₂O.2HCl, is closely related. Bunsen's "basic chlorcacodyl" and "cacodyl superchloride" were shown by Baeyer to be, respectively, a mixture of cacodyl oxide with cacodyl chloride, and (CH₃)₂As(OH)Cl₂.

¹⁰ Compare this reaction with that of mercurous chloride and dimethylarsine. Am. Chem. J., 35, 35 (1906).

cacodyl hydroxide.¹¹ Its solubility in water and easy decomposition by acids and alkalies suggests its possible usefulness in therapeutics. The yield when the substance was prepared above was about 20%. When 1 g. of magnesium oxide was added to 20 g. of the initial additive compound in 400 cc. of water, a 42% yield was obtained. With 2 g. of magnesium oxide, however, no yield at all was obtained. When the 1 g. of magnesium oxide was replaced by 2.5 g. of calcium carbonate, a 61% yield was recovered, but with 5 g. of calcium carbonate no yield was obtained. These experiments show that one molecular equivalent of alkali leads to a maximum yield, but two molecular equivalents destroy it.

Cuprous Chloride.—When 1.5 g. of anhydrous cuprous chloride and 2.4 g. of cacodyl chloride were brought together under petroleum ether, the mixture shaken and permitted to stand, a white additive compound was formed. It was filtered, washed with petroleum ether and dried in a vacuum.

Analysis. Calc. for (CH₃)₂AsCl.2CuCl: Cl, 31.42. Found: 31.79.

Cupric Chloride.—When equal weights of anhydrous cupric chloride and cacodyl chloride were brought together in petroleum ether, a dark gray-green, additive compound was formed.

Analysis. Calc. for (CH₃)₂AsCl.CuCl₂: Cl, 38.69. Found: 39.19.

The substitution of ordinary ether for the petroleum ether in this preparation yielded a white hydrolytic product. 12 

Analysis. Calc. for (CH₃)₂AsOH.CuCl₂: Cl, 27.64. Found: 27.70.

When the anhydrous cupric chloride and cacodyl chloride were brought together in absolute ether, the gray product first formed changed to tan and finally to white. Ethyl chloride was found in the reaction ether.

Analysis. Calc. for [(CH₃)₂As]₂O.2CuCl₂: Cl, 28.65. Found: 28.66.

Ferric Chloride.—A mixture of equimolecular quantities of cacodyl chloride and ferric chloride was allowed to stand for months in absolute ether. Green crystals of ferrous chloride were deposited. That the ether contained (CH₃)₂AsCl₃, was proved by its hydrolysis of the latter to caeodylic acid.

# Summary

Methods are described for the preparation of the bromide, iodide and cyanide of cacodyl and of basic cacodyl chloride, from the chloride. Bunsen's work on "Mercuric chloride cacodyl oxide" has been reinvestigated and the new data are presented. Four new compounds of cacodyl chloride and the copper chlorides are described.

SEATTLE, WASHINGTON

This formula, however, is disproved by the molecular weight and by Bunsen's own analytical data.

Analyses. Calc. for  $(CH_3)_2AsCI(OH)HgCl$ : C, 6.09; H, 1.80; Cl, 18.02; Hg, 50.97. Calc. for  $[(CH_3)_2As]_2O.2HgCl_2$ : C, 6.24; H, 1.57; Cl, 18.44; Hg, 50.17. Found (by Bunsen): C, 6.25; H, 10.76; Cl, 18.01; Hg, 50.76.

It is formed by hydrolysis of the initial additive compound of Bunsen. See Am. Chem. J., 40, 127 (1908).

¹² See Ostwald, Ref. 1, p. 77, for the instability of Bunsen's compound prepared from cacodyl oxide, hydrochloric acid and cuprous chloride.

¹¹ This compound agrees in all of its properties with the "Mercuric chloride cacodyl oxide" prepared by Bunsen:  $[(CH_3)_2As]_2O + 2HgCl_2 \longrightarrow [(CH_3)_2As]_2O.2HgCl_2$ .

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]
A FURTHER STUDY OF THE NEUTRAL AMMONIUM SALTS OF
SOME ORGANIC ACIDS AND THEIR SUBSTITUTED
DERIVATIVES

Eighth Communication¹

By LeRoy McMaster and Paul K. Pratte Received July 2, 1923

This work is a continuation of the investigation which has been in progress in this Laboratory on the preparation and properties of the neutral ammonium salts of organic acids and their substituted derivatives. The salts described in this paper were, with slight modifications in several instances, prepared by the same general method as was used in the previous investigations, that is, by passing dry ammonia into solutions of the acids in those anhydrous organic solvents in which their salts were found to be insoluble. When it was found that an acid and its ammonium salt were both soluble in a certain solvent, the solution of the ammonium salt was poured into an excess of another solvent in which the salt was insoluble. In several cases it was necessary to evaporate the solutions nearly to dryness before the salts crystallized. In the case of acetyl m-aminobenzoic acid, it is insoluble in all the common organic solvents that do not react with ammonia and its solubility in water is very slight. It is soluble in concd. ammonium hydroxide. The neutral ammonium salt was thus prepared by dissolving the acid in coned. ammonium hydroxide, evaporating the solution to dryness, and then passing ammonia into an alcoholic suspension of the residue.

Of the neutral salts described in this paper none has been previously prepared except those of phenoxyacetic acid² and 2,5-dichlorobenzene sulfonic acid.³ They were prepared by neutralizing an aqueous solution of the acid with ammonium hydroxide. The ammonium 1,2,4-dinitro benzoate was described in a previous paper,⁴ but we have determined its solubilities and recorded them in this work.

Solubility determinations were made of only the stable salts by the analytical method. By this method the salt, in excess, was stirred with the solvent at a definite temperature until equilibrium was reached. The excess of salt was allowed to settle and the clear liquid decanted off into a weighed evaporating dish and immediately weighed. When the solvent had completely evaporated the evaporating dish was again weighed. From the differences in weight the amount of salt soluble in the solvent at the given temperature could be calculated. All the solubility determinations.

- 1 For a list of the previous papers on this subject see This Journal, 40, 683 (1918).
- ² Fritzsche, J. prakt. Chem., [2] 20, 269 (1879).
- ³ Lesimple, Z. Chem., 4, 226 (1868).
- McMaster and Wright, This Journal, 40, 683 (1918).

nations were carried out at  $20^{\circ}$ , which temperature was maintained in an automatic water thermostat. A large test-tube was used to hold the solubility mixture and was fitted at the top with a mercury seal to prevent the absorption of water vapor from the air by the solvent. This seal was constructed by sinking a piece of glass tubing (a 25mm, section of a large test-tube) into a cork containing a glass bearing for the stirrer. The space between the tube and the bearing was then filled with mercury. A second tube, smaller than the first, was then tightly fastened to the stirring rod by means of a cork so that when the stirrer extended to the bottom of the test-tube, the second tube fitted within the bearing and the large tube at the same time dipped below the surface of the mercury. In this manner the contents of the test-tube could be sealed against contact with air and at the same time the solution thoroughly stirred at about 200 r.p.m. It was found by experiment that 20 minutes was sufficient to bring the

Table I
Properties and Analyses of Neutral Ammonium Salts

	Stability in		Nitr	rogen	
A	dry air (+ = stable:	moist air	Cale.	Found	
	• •	- = unsta	, ,,	%	
Iodo-acetic			6.89	6.90	
Phenoxyacetic	+	+	8.28	8.29	
p-Nitrophenylacetic	+	+	14.14	14.08	
$\beta$ -Bromopropionie		a	8.23	7.98	
α-Bromo-n-butyric		a	7.61	7.48	
o-Iodobenzoic	+	-	5.28	5.30	
p-Iodobenzoic			5.28	5.24	
o-Methoxybenzoic	+	+	8.28	9.32	
Acetyl m-aminobenzoic		****	14.28	14.19	
Acetyl p-aminobenzoic		steek	14.28	14.30	
5-Nitrosalicylie	+	+	14.00	14.00	
α-Naphthalenesulfonic	+	-	6.22	6.28	
β-Naphthalenesulfonic	+	+	6.22	6.26	
2,5-Dichloro-benzenesulfonic	+	+	5.74	5.70	
4-Nitrochloro-benzene-2-sulfonic	+	+	11.00	11.00	
a Delignescent					

Deliquescent.

TABLE II SOLUBILITIES OF NEUTRAL AMMONIUM SALTS

	Solvent				
Acid	Water		$C_2H_bOH$		
Phenoxyacetic	13.03	3.97	0.44		
p-Nitrophenylacetic	7.41	15,14	1.82		
o-Iodobenzoic	67.11	184.10	63.37		
o-Methoxybenzoic	38.25	17.85	4.82		
1,2,4-Dinitrobenzoic	62.70	21.39	3.85		
5-Nitrosalicylic		4.41	1.96		
α-Naphthalenesulfonic	45.91	34.45	9.22		
β-Naphthalenesulfonic	11.71	8.33	2.53		
2,5-Dichloro-benzenesulfonic	11.30	20.15	2.59		
4-Nitrochloro-benzene-2-sulfonic	4.72	2.76	0.96		

solution to equilibrium with the salt. The solubilities so found are expressed in grams of salt per hundred grams of solvent.

In the preceding tables are recorded several of the properties, the results of analysis and the solubilities of the neutral ammonium salts of the acids listed.

# Summary

Fifteen neutral ammonium salts of organic acids have been prepared by the action of dry ammonia on solutions of the respective acids.

The stabilities in dry and moist air and some of the solubilities have been determined.

St. Louis, Missouri

[Contribution from the Chemical Laboratory, University of Texas]

#### REDUCTION OF SEMICARBAZONES

By E. J. Poth and J. R. Bailey Received August 8, 1923

#### Introduction

The Skita method of reduction with colloidal platinum as catalyst, as shown in a previous communication from this Laboratory, is of service in converting semicarbazones to the corresponding semicarbazides where other methods of reduction have produced only negative results. Certain semicarbazones, such as glyoxylic acid semicarbazone and benzal semicarbazone, are readily reduced with sodium amalgam without molecular cleavage, but it has been quite definitely determined that reduction in the desired way with sodium amalgam succeeds only when an electronegative radical is joined to the carbon of the C—N complex. From the experiments described in this paper it appears probable that catalytic reduction with colloidal platinum is of general application in the conversion of semicarbazones to the corresponding semicarbazides.

Conditions have been established for obtaining excellent yields of semicarbazides with a minimum amount of platinum; for example, carvone semicarbazone and hexanone semicarbazone can be reduced with a yield of 80% where the semicarbazone and 10% platinic chloride solution are employed in the ratio of  $10~\rm g$ . to  $1~\rm cc$ . It is necessary in the case of camphor and fenchone, terpene ketones of similar structure, to employ for the reduction of their semicarbazones a much larger amount of platinic chloride. Camphor

- ¹ Neighbors, Foster, Clark, Miller and Bailey, This Journal, 44, 1557 (1922).
- ² Rupe and Oestreicher, Ber., 45, 30 (1912).
- ³ Darapsky and Prabhakar, Ber., 45, 2625 (1912). Bailey and Read, This Journal, 36, 1751 (1914).
  - 4 Kessler and Rupe, Ber., 45, 26 (1912).

semicarbazone and platinic chloride are employed in the ratio of  $1\,\mathrm{g}$ . to  $1\,\mathrm{cc}$ , while in the case of fenchone semicarbazone the ratio is  $1\,\mathrm{g}$ . to  $4\,\mathrm{cc}$ .

It has been found in the catalytic reduction of the C-N complex to form basic products that the reduction is greatly facilitated by the presence of an acid for salification, but the reductions described on different semicarbazones, as shown in the experimental part of this article, give maximum yields with great variations in the amount of hydrochloric acid present. In the reduction of hexanone semicarbazone the hydrochloric acid, liberated from the platinic chloride used, suffices for a completion of the reaction, although this represents only a small fraction of the acid required for converting the hexahydrophenyl semicarbazide formed to its hydrochloride. With carvone, camphor and menthone semicarbazones maximum vields are obtained when only half of the calculated amount of hydrochloric acid is present, whereas in the case of acctone and fenchone semicarbazones it is necessary to employ the calculated amount of hydrochloric acid. The advantage of using a minimum amount of hydrochloric acid, in the case of the semicarbazones that readily hydrolyze, is apparent but, on the other hand, where the semicarbazide is difficultly, and its hydrochloride readily, soluble, a sufficiency of the mineral acid has the advantage of effecting clear solution at the end of the reduction. In order to keep down the acid concentration, it will frequently be found advisable to add the hydrochloric acid gradually at different stages of the reduction. Of the semicarbazones investigated, the velocity of hydrogenation is greatest in the case of those of hexanone, carvone and acetone, and slowest in that of fenchone, while camphor and menthone semicarbazones, in the order named, follow fenchone semicarbazone in their slowness of reduction. The effect of temperature here has not been studied, but it is quite evident that at higher temperatures there would be danger of increased hydrolvsis of the semicarbazones.

The reduction of carvone semicarbazone is of interest because it contains two double bonds between carbons and a third between a carbon and a nitrogen. It is certain that the reduction of the C=N complex does not precede that of the C=C complexes, because, with one-third of the calculated hydrogen consumed, there remains, even with one molecular equivalent of hydrochloric acid present, a large amount of insoluble semicarbazone. The indications are that the difference in velocities of the reduction of the unsaturated complexes is not sufficient to allow of isolation of partial reduction products of carvone semicarbazone, at least with satisfactory yields. However, no experiments were made in this direction.

The aliphatic and hydro-aromatic semicarbazides, in contrast to the aryl

⁵ Compare A. Skita, *Ber.*, **52**, 1521 (1919). Lochte, Bailey and Noyes, This Journal, **43**, 2599 (1921).

semicarbazides, form stable salts that do not lose hydrochloric acid on standing. However, the hydrochlorides in aqueous solution react acid to methyl orange. All semicarbazides add a molecule of phenyl isocyanate and with acid chlorides yield acyl derivatives which with caustic alkalies lose a molecule of water to form triazoles.6 They apparently react with phenyl mustard oil, but the products could not be made to crystallize. The hydro-aromatic semicarbazides react with nitrous acid, but crystalline nitroso compounds were not isolated. On oxidation this type of semicarbazides yields azo compounds that cannot be isolated because of the ease with which they invariably transpose to the isomeric, colorless semicarbazones.7 All of the hydro-aromatic semicarbazides investigated give waterinsoluble condensation products with formaldehyde8 which possess various solubilities in organic solvents and are neutral to both acids and alkalies. In no instance was a way of recrystallizing these substances found. Experiments aimed at acid and alkali hydrolysis of the hydro-aromatic semicarbazides to the corresponding hydrazino compounds did not produce the desired results. The decomposition of hexahydrophenyl semicarbazide at elevated temperatures is discussed in the succeeding article.

# Experimental Part

General Conditions for Reduction of Semicarbazones.-In the case of most semicarbazones, it is advisable to prepare the colloidal platinum solution before the addition of the substance to be reduced. To a mixture of 200 cc. of water, 100 cc. of methyl alcohol, 5 cc. of 10% chloroplatinic acid and a few drops of seeding solution is added 0.4 g. of gum arabic, and the mixture is shaken in the usual way with hydrogen under pressure until a deep black color develops. A grayish, colloidal solution at this stage indicates a catalyst of poor efficiency and should not be used, since the physical state of the colloid has a pronounced effect on the rate of hydrogenation and the yield of semicarbazide. The semicarbazone is next added to the platinum solution, followed by the requisite amount of hydrochloric acid, and the reduction carried out with agitation in the usual way with an initial pressure of hydrogen registering  $2^{1}/_{3}$  atmospheres (35 lbs.). is advisable to hydrogenate semicarbazones with a pressure never lower than  $1^2/_3$  atmospheres (25 lbs.). In the reductions described, 33% alcohol was employed as solvent with the ratio of solvent to platinic chloride of 60 cc. to 1 cc. In all cases except that of benzal semicarbazone 1 g. of semicarbazone was reduced in 6 cc. of the colloidal solution. As a rule, semicar-

^a Compare Widman, Ber., 29, 1946 (1896). Bailey and Acree, ibid., 33, 1520 (1900). Ref. 2, p. 32.

⁷ Compare Elbers, Ann., 227, 354 (1885). E. Fischer, Ber., 29, 894 (1896). Thiele, Ann., 376, 267 (1910). Ref. 1, p. 1561.

⁸ Compare Rassow, J. prakt. Chem., [2] 64, 131 (1901). Knorr and Weidel, Ber., 42, 3525 (1909).

bazones and, unless present as hydrochlorides, many semicarbazides are not completely soluble in this concentration of alcohol. A higher concentration is objectionable because, frequently, it breaks the colloid and in any event has a tendency to inactivate the catalyst.

The general method of procedure in carrying out the reduction of semicarbazones and the isolation of the semicarbazide formed is given under the preparation of fenchyl semicarbazide. The additional data in the following table are self-explanatory.

TABLE I
HYDROGENATION EXPERIMENTS

Semicarbazide formed	Semicar- bazone G.	Methyl alcohol Cc.	Water Ce.	HC1a	Pt sol. Cc.	Time Hours	Yield %
Fenchyl	10	50	10	calc.	43	24	100
Carvomenthyl	50	100	200	$^{1}/_{2}$ calc.	5	5	80
Hexahydrophenyl	50	100	200	trace	5	3	80
Menthyl	50	100	200	$^{1}/_{2}$ calc.	5	2.75	80
isoPropyl	50	100	200	cale.b	5	6	76
Benzyl	25	100	200	cale.	5	2.5	50
Bornyi	10	20	40	$^{1}/_{2}$ calc.	10	20	100

^a Coned, hydrochloric acid was used so as to keep the volume of solution a minimum.

In all the reduction experiments 0.4 g. of gum arabic was used as a protective colloid for each 300 cc. of colloidal solution.

Fenchyl Semicarbazide.—To 43 cc. of 10% chloroplatinic acid, in a pressure bottle, are added 0.5 g. of gum arabic in 10 cc. of water, a few drops of seeding colloid, 50 cc. of methyl alcohol, 1 cc. of hydrochloric acid (d., 1.2) and 10 g. of fenchone semicarbazone, and the mixture is then shaken at over 2 atmospheres' pressure until the theoretical amount of hydrogen is absorbed. Finally, the colloid is broken with acetone, the filtered solution evaporated in a vacuum on a water-bath, and the fenchyl semicarbazide precipitated with ammonium hydroxide. Conditions have not been established for isolating salts of fenchyl semicarbazide which, so far as examined, do not possess good crystallizing properties. Fenchyl semicarbazide is practically insoluble in water, ether and petroleum ether, readily soluble in dilute mineral acids, chloroform and ethyl alcohol, slightly soluble in benzene and moderately soluble in acetic ether. It dissolves in glacial acetic acid but precipitates on dilution. For purification, it can be recrystallized from ethyl acetate in short needles, melting at 181° with decomposition.

Analyses. Calc. for  $C_{11}H_{21}ON_3$ : C, 62.56; H, 9.95; N, 19.91. Found: C, 62.51; H, 10.25; N, 20.02.

Benzoyl-fenchyl Semicarbazide,  $C_{10}H_{17}N(COC_6H_5)NHCONH_2$ .—To 5 g. of fenchyl semicarbazide, dissolved in 300 cc. of dry benzene, are added 4 cc. of benzoyl chloride and 5.3 g. of sodium bicarbonate. After the mixture has been refluxed for four hours on a

^b The acid was added in three equal portions, one at the beginning and the other two when the hydrogen absorbed equalled  $^{1}/_{3}$  and  $^{2}/_{3}$ , respectively, of the amount required.

^c This semicarbazone was not isolated, but benzaldehyde and semicarbazide hydrochloride, in calculated amounts, were added to the reduction mixture.

⁹ Wallach, Ann., 353, 211 (1907).

boiling water-bath, the benzoyl derivative separates as a gelatinous mass. The solvent is then distilled and the residue extracted with 95% alcohol. From the alcoholic solution, the benzoyl derivative is precipitated on dilution. On recrystallization from glacial acetic acid containing a few drops of water, it is obtained as a fine, crystalline powder which softens at 223° and decomposes at 226°. Like the other benzoyl derivatives described in this paper, it has neither acidic nor basic properties. An analysis of a sample, dried at  $106^{\circ}$ , indicates that the product obtained was not pure.

Analyses. Calc. for  $C_{18}H_{25}O_2N_3$ : C, 68.57; H, 7.94; N, 13.33. Found: C, 68.02; H, 8.39; N, 13.31, 13.36.

3-Hydroxy-1-fenchyl-5-phenyltriazole.—When 2.85 g. of benzoyl-fenchyl semicarbazide is boiled for one-half hour with 40 cc. of 30% potassium hydroxide, the triazole in the form of its potassium salt separates as an oil and redissolves on dilution. The triazole is liberated with hydrochloric acid and extracted with ether. It is readily soluble in water, alcohol or glacial acetic acid, slightly soluble in acetic ether or benzene, and insoluble in the other common solvents. Recrystallized from 95% ethyl alcohol, the triazole forms thick, triangular plates, which soften at 230° and melt at 234° to a clear, light brown liquid.

Analyses. Calc. for  $C_{18}H_{23}ON_3$ : C, 72.73; H, 7.74; N, 14.14. Found: C, 72.57, 72.79, 72.60; H, 8.00, 8.06, 7.67; N, 14.36, 14.38.

 $\alpha$ -Phenylcarbamyl-fenchyl Semicarbazide,  $C_{10}H_{17}N(CONHC_6H_6)$ —NHCONH2.—A solution of 4 g. of fenchyl semicarbazide and 2.4 cc. of phenyl isocyanate in 80 cc. of dry benzene is refluxed on a water-bath for one hour. The urethan separates and is recrystallized from 95% ethyl alcohol in the form of thin, shaft-like plates with arched end-faces, melting to a clear liquid at 192°. Like the other carbamyl derivatives described in this paper, it has neither acidic nor basic properties.

Analyses. Calc. for  $C_{18}H_{26}O_2N_4$ : C, 65.45; H, 7.88; N, 16.97. Found: C, 65.33; H, 7.93; N, 17.23.

Carvomenthyl Semicarbazide.—This semicarbazide prepared from carvone semicarbazone, ¹⁰ is readily soluble in the common solvents with the exception of water, ether, and petroleum ether. It separates from ethyl acetate in thin plates melting with slow gas evolution at 126°.

Analyses. Calc. for C₁₁H₂₃ON₃: C, 61.97; H, 10.79; N, 19.72. Found: C, 62.06; H, 11.02; N, 19.98.

Carvone semicarbazone is obtained in a yield of 73% by adding 7 cc. of carvone in 25 cc. of ethyl alcohol to a solution of 5 g. of semicarbazide hydrochloride and 5 g. of anhydrous sodium acetate in 10 cc. of water. After 12 hours the semicarbazone is filtered off and washed with water, alcohol, and ether.

Carvomenthyl Semicarbazide Hydrochloride.—The hydrochloride separates from the reduction mixture of carvone semicarbazone on concentration. Recrystallized from 95% alcohol, it is obtained in the form of short needles that decompose at 186°. This salt is readily soluble in alcohol and water, and very difficultly soluble in the other common solvents.

Analyses. Calc. for C₁₁H₂₄ON₃Cl: N, 16.83; Cl, 14.23. Found: N, 17.13; Cl, 13.99.

Benzoyl-carvomenthyl Semicarbazide.—The procedure here is the same as in the case of the corresponding fenchyl compound, except that only 70 cc. of benzene is employed to 5 g. of the semicarbazide. When the reaction is completed, one-half of the solvent is distilled, and after the addition of 200 cc. of petroleum ether the mixture is

¹⁰ Rupe and Dorschky, Ber., 39, 2113 (1906).

refluxed for one hour. In this way the benzoyl compound is obtained in a suitable state for filtering. Recrystallized from glacial acetic acid containing a few drops of water, it melts to a clear liquid at 235°. It is either difficultly soluble or insoluble in the common solvents.

Analyses. Calc. for  $C_8H_{27}O_2N_3$ : C, 68.14; H, 8.51; N, 13.25. Found: C, 67.82; H, 8.70; N, 13.35.

3-Hydroxy-1-carvomenthyl-5-phenyltriazole.—This triazole, prepared in the usual way, can be isolated, in the form of an oil, by means of extraction with chloroform. When this oil is taken up in alcohol and diluted with water, the triazole separates in a crystalline form by allowing the solution to evaporate at room temperature. It has solubilities similar to those of the corresponding fenchyl triazole, and crystallizes from absolute alcohol in thin plates that begin to soften at 180°, and melt completely at 187°.

Analyses. Calc. for  $C_{18}H_{25}ON_3$ : C, 72.24; H, 8.36; N, 14.05. Found: C, 72.14; H, 8.63; N, 14.27.

 $\alpha$ -Phenylcarbamyl-carvomenthyl Semicarbazide, prepared in benzene solution under the same conditions as the corresponding fenchyl derivative is, after removal of the greater part of the solvent, refluxed with petroleum ether, filtered off, and recrystallized from acetic acid containing a few drops of water. It is thus obtained in clusters of radiating needles that begin to soften at 202°, and melt at 205° with gas evolution. This derivative is readily soluble in glacial acetic acid and difficultly soluble in other common solvents.

Analyses. Calc. for  $C_{18}H_{28}O_{2}N_{4}$ : C, 65.06; H, 8.43; N, 16.87. Found: C, 65.21; H, 8.79; N, 17.05.

The Action of Formaldehyde on Carvomenthyl Semicarbazide Hydrochloride.—When an aqueous solution of carvomenthyl semicarbazide is treated with an excess of formalin, a white crystalline product separates immediately that is very soluble in the common organic solvents with the exception of petroleum ether. Since no method of purifying this substance by recrystallization was found, the sample for analysis was thoroughly washed with water and dried at room temperature in a vacuum. It begins to decompose with evolution of ammonia at about 125° and melts with further decomposition at 150°. The analysis indicates that in the above reaction a molecule of water is split out between one molecule of formaldehyde and two molecules of the semicarbazide. A probable structure of this substance is, therefore,  $CH_2(N(NHCONH_2)C_{10}H_{19})_2$ ,

Analyses. Calc. for  $C_{23}H_{46}O_2N_6$ : C, 63.01; H, 10.50; N, 19.18. Found: C, 62.79; H, 10.21; N, 18.41.

Hexahydrophenyl Semicarbazide.—After the solution obtained in the reduction of hexanone semicarbazone has been concentrated and chilled, it hexahydrophenyl semicarbazide hydrochloride separates as large acicular crystals, or the free base may be precipitated with ammonia. The base is readily soluble in alcohol, slightly soluble in ethyl acetate or benzene, and difficultly soluble in the other common solvents. Recrystallized from 95% ethyl alcohol, as fine needles, it softens at 183° and decomposes at 185° with evolution of gas.

Analyses. Calc. for  $C_7H_{15}ON_3$ : C, 53.50; H, 9.55; N, 26.75. Found: C, 53.46; H, 9.85; N, 26.87.

The hydrochloride recrystallizes from alcohol in long, slender needles melting at 176° to 178°.

Analyses. Calc. for C₇H₁₆ON₃Cl: N, 21.70; Cl, 18.35. Found: N, 21.85; Cl, 18.53.

¹¹ Zelinsky, Ber., 30, 1541 (1897).

Benzoyl-hexahydrophenyl Semicarbazide.—The conditions employed in the preparation and isolation of benzoyl-carvomenthyl semicarbazide are followed in this preparation. This benzoyl derivative is readily soluble in glacial acetic acid, moderately soluble in alcohol, chloroform or acetone, and difficultly soluble in the other common solvents. It can be recrystallized from 95% acetic acid in the form of fine needles, which begin to soften at 260°, and melt with slow evolution of gas at 267°.

Analyses. Calc. for  $C_{14}H_{19}O_2N_3$ : C, 64.33; H, 7.33; N, 16.08. Found: C, 64.30; H, 7.61; N, 16.28.

3-Hydroxy-1-hexahydrophenyl-5-phenyltriazole.—This triazole is prepared and isolated as was the corresponding carvomenthyl compound. It is very soluble in chloroform, less soluble in alcohol, slightly soluble in ethyl acetate, and very difficultly soluble in the other common solvents. It separates from alcohol in radiating clusters of slender prisms with pyramidal end-faces, and melts to a light brown liquid at 232–234°.

Analyses. Calc. for  $C_{14}H_{17}ON_3$ : C, 69.13; H, 7.00; N, 17.28. Found: C, 69.15; H, 7.33; N, 17.23.

 $\alpha$ -Phenylcarbamyl-hexahydrophenyl Semicarbazide, prepared in benzene solution under conditions analogous to those for the corresponding carvomenthyl derivative, is recrystallized from 95% alcohol as short microscopic needles, which decompose with vigorous gas evolution at 236°. It is slightly soluble in ethyl acetate, chloroform, and acetone.

Analyses. Calc. for  $C_{14}H_{20}O_2N_4$ : C, 60.87; H, 7.25; N, 20.29. Found: C, 60.80; H, 7.55; N, 20.53.

Benzyl Semicarbazide.—Benzyl semicarbazide was originally prepared by Kessler and Rupe by reducing benzal semicarbazone with sodium amalgam.  12  It can be made in a simple way by catalytic reduction of a mixture of semicarbazide hydrochloride and benzaldehyde in molecular proportions. However, the yield under the conditions employed is only 50% of that calculated.

# isoPropyl, Bornyl, and Menthyl Semicarbazides13

Under the conditions given above for reducing acetone semicarbazone, only  $^{1}/_{30}$  as much platinum is required as recommended by Neighbors and Bailey, with a slight increase in yield of iso-propyl semicarbazide. In the isolation of this semicarbazide with chloroform, continuous extraction is recommended. Our method of reducing camphor semicarbazone gives a quantitative yield of bornyl semicarbazide and employs only one-third of the amount of platinum used by Miller and Bailey. In reducing menthone semicarbazone,  $^{1}/_{27}$  of the platinum employed by Clark and Bailey is used, and the time consumed in the process is appreciably shortened. Attention is directed to the fact that menthyl semicarbazide hydrochloride is difficultly soluble in the common solvents. It is, therefore, advisable at the end of the reduction to filter off the hydrochloride before breaking the colloid. Any dissolved menthyl semicarbazide is recovered in the usual way.

Benzoyl Menthyl Semicarbazide.—This benzoyl derivative has poor crystallizing properties. For analysis it was purified by precipitation from its alcoholic solution with ethyl acetate as a crystalline powder melting with gas evolution at 216°.

Analysis. Calc. for C₁₈H₂₇O₂N₈: N, 13.25. Found: N, 13.50.

 $\alpha$ -Phenylcarbamyl-menthyl Semicarbazide, prepared like the corresponding carvomenthyl compound, crystallizes from alcohol in clusters of radiating needles, which decompose at 184°.

¹² Ref. 4, p. 26.

¹⁸ Ref. 1, pp. 1559, 1563.

Analyses. Calc. for  $C_{18}H_{28}O_2N_4$ : C, 65.06; H, 8.43; N, 16.87. Found: C, 65.09; H, 8.55; N, 17.21.

# Summary

- 1. Conditions are given for obtaining good yields of hydro-aromatic semicarbazides by catalytic reduction of the corresponding semicarbazones.
- 2. The catalytic reduction of acetone semicarbazone to *iso*-propyl semicarbazide has been simplified.
- 3. It is made probable that for the first time a method of general application has been found in catalytic reduction for the conversion of semicarbazones to the corresponding semicarbazides.
- 4. Terpene semicarbazides being now readily available, a pharmacological study of the heterocyclic compounds that can be made from these should prove of interest.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TEXAS]

# THE BEHAVIOR OF SEMICARBAZIDES AT ELEVATED TEMPERATURES

By E. J. Poth and J. R. Bailey Received August 8, 1923

#### Introduction

Hexahydrophenyl semicarbazide, described in the preceding article decomposes at elevated temperatures, forming dihexahydrophenyl carbazide (I), hexahydrophenyl urazole (II), and dihexahydrophenyl urazine (III),

substances described in the experimental part of this paper. It is evident that in the formation of I, a molecule of urea is split out between two molecules of the semicarbazide, and that II results from the interaction of this urea with a third molecule of the semicarbazide, while if the structure of our urazine is correctly interpreted by Formula III, its formation is entirely independent of the reactions involved in connection with I and II.

Pinner¹ studied the effect of heat on phenyl semicarbazide and reported that at a temperature of 160–170° there are given off carbon dioxide, carbon monoxide and benzene, while the nonvolatile residue consists of unchanged phenyl semicarbazide, phenyl urazole, and diphenyl urazine. In repeating the experiment of Pinner, we find that ammonia, nitrogen and carbon dioxide, but not carbon monoxide, are evolved. What is more important

¹ Pinner, Ber., 21, 1224 (1888).

is the proof that diphenyl carbazide2 is also formed, although its isolation and analysis here were not effected. Through the remarkable color reactions of this substance reported by Cazeneuve3 it can now be identified in the minutest traces and, furthermore, as observed by Skinner and Ruhemann, this carbazide imparts through atmospheric oxidation to ammonium hydroxide solution within a short time a deep red color due to the formation of the so-called diphenyl carbazone, 4 C₆H₅N=NCONHNH- $C_6H_5$ . We find that phenyl semicarbazide, on the other hand, imparts to ammonium hydroxide solution a vellow color and gives none of the Cazeneuve color reaction of the carbazide. That diphenyl carbazide is formed at least in small amount, even on fusion of phenyl semicarbazide, can be demonstrated in a simple way by heating a very small sample of the latter substance in an ordinary melting-point tube to liquefaction, then immediately removing the tube from the bath, and carrying out the color tests referred to above. As is evident from the following equations, the formation of diphenyl carbazide, as a decomposition product of phenyl semicarbazide, clears up the mechanism of the simultaneous formation here of phenyl urazole.

$$2 C_{6}H_{5}NHNHCONH_{2} + \delta = (C_{6}H_{6}NHNH)_{2}CO + CO(NH_{2})_{2}$$

$$N-C_{6}H_{5}$$

$$C_{6}H_{5}NHNHCONH_{2} + CO(NH_{2})_{2} = CO NH + 2NH_{3}$$
(2)

The structure of Pinner's so-called diphenyl urazine was first correctly interpreted by  $Heller^5$  as  $C_6H_5-N$ —NH-CO and this formula has

been confirmed by the work of other investigators.6

As might be expected, dihexahydrophenyl carbazide does not give color reactions analogous to diphenyl carbazide. An explanation of this difference in behavior of the two carbazides is evident from the following considerations. All the color reactions of diphenyl carbazide depend primarily on the oxidation of this hydrazo body to a mixed hydrazo-azo compound containing the group, —N=N—CO—NHNH—. In the hydrazo complex of this group the imido hydrogens are replaceable by metals with the formation of colored salts that possess the unusual property of being soluble in organic solvents. On the other hand, dihexahydrophenyl carbazide contains the group CO(NHNHCH=)2, and it is well known that the stable oxidation product expected here would be of hydrazono and not azo structure.

- ² Skinner and Ruhemann, J. Chem. Soc., 53, 550 (1888).
- ³ Cazeneuve, Chem.-Zig., 24, 557, 684 (1900).
- 4 Heller, Ann., 263, 274 (1891).
- 5 Ref. 4, p. 282.
- 6 Freund and Kuh, Ber., 23, 2831 (1890). Rolla, Gazz. chim. ital., 38, 344 (1908).
- ⁷ Poth and Bailey, This Journal, 45, 3003 (1923).

It is probable that the system, 2 mols. of semicarbazide  $\stackrel{\frown}{}$  1 mol. of carbazide + 1 mol. of urea, represents a reversible reaction. In conformity with this view is the observation of Skinner and Ruhemann⁸ that phenyl semicarbazide is formed on heating a mixture of diphenyl carbazide and urea. In the case of the phenyl compounds the equilibrium shifts to the left, while with hexahydrophenyl compounds it shifts to the right, so that in the latter case conditions have been established for obtaining a fairly good yield of carbazide by heating the semicarbazide.

The very unexpected observation was made that hexahydrophenyl semicarbazide on heating with urethan forms the carbazide in good yield. Apparently, the action of the urethane is either catalytic or, what is more probable, the urethan simply exerts a solvent action, causing a liquefaction of the semicarbazide at a temperature lower than its melting point. This latter view is in accordance with our observation that protracted heating of the semicarbazide melt or the urethan-semicarbazide melt has a marked influence in decreasing the yield of carbazide, due probably to its gradual decomposition at elevated temperatures. This method of preparing dihexahydrophenyl carbazide, applied to *i*-propyl and phenyl semicarbazides, showed that here urethan has no effect on the carbazide formation, at least under the conditions of our experiments.

# Experimental Part

The Decomposition of Hexahydrophenyl Semicarbazide at Elevated Temperatures.—The semicarbazide, heated for 11/2 hours at 180-185°, decomposes, giving a strong odor of ammonia and an aromatic odor resembling cyclohexanol. The melt, of a slightly yellow color, is extracted with 50 cc. of boiling water and filtered. From the filtrate there separates a white crystalline product, which is filtered off, and the filtrate is again used for extracting the residue. In all, three extractions are made with the same solution. The water-soluble material is leached out with a little chloroform to remove carbazide and urazine present only in small amounts, the residue dissolved in ammonia, and the urazole precipitated from the filtered solution with acetic acid. For further purification it is recrystallized from water. The yield of urazole is about 13.8% of that calculated theoretically. The water-insoluble product obtained above dissolves in ammonia, thus showing the absence of unchanged semicarbazide, and reprecipitates with acetic acid. It is purified by recrystallization from alcohol. The yield of urazine is about 34%. The carbazide, which under the above conditions is formed in very small amount, is dissolved in acetic acid and reprecipitated with ammonia with subsequent recrystallizations from water and acetic ether. Complete analyses of the above products agree closely in each case with the formula assigned.

⁸ Skinner and Ruhemann, Ber., 20, 3373 (1887).

If the semicarbazide is quickly heated up to  $200^{\circ}$ , 12 minutes being consumed in the operation, all the water-soluble material dissolves in dil. hydrochloric acid, thus showing the absence of urazole, and the carbazide is obtained from the acid solution by precipitation with ammonia in a yield of 41%. As the water-insoluble material is completely soluble in acid, it contains no urazine, but is unchanged semicarbazide. The amount recovered amounted to 19.5% of that originally used in the experiment.

Dihexahydrophenyl Carbazide.—The carbazide is readily soluble in cold chloroform or alcohol. Recrystallized from water, it is obtained in plates that melt at 187°. Acetic ether is also well adapted for recrystallizing the carbazide, which is difficultly soluble in benzene and sparingly soluble in ether. This substance acts as a strong reducing agent.

Analyses. Calc. for  $C_{13}H_{26}ON_4$ : C, 61.42; H, 10.23; N, 22.05. Found: C, 61.38; H, 10.34; N, 22.19.

Dihexahydrophenyl carbazide hydrochloride separates on dissolving the carbazide in methyl alcoholic hydrochloric acid in the form of thin plates, melting with gas evolution at 217°.

Analyses. Calc. for C₁₃H₂₈ON₄Cl₂: N, 17.12; Cl, 21.47. Found: N, 17.18; Cl, 21.76.

The most satisfactory method of preparing dihexahydrophenyl carbazide from the corresponding semicarbazide is to heat the latter mixed with 1/2 its weight of urethan at 160° until liquefaction ensues and then maintain a temperature of 150° for 15 minutes. In this way an almost completely water-soluble melt is obtained which, worked up in the way described, gives a yield of 73% of carbazide. In an experiment where the mixture of semicarbazide and urethan was heated at 165° for  $1^1/2$  hours, only a 20% yield of carbazide was obtained.

Phenyl semicarbazide and i-propyl semicarbazide, heated with urethan under conditions similar to those employed in the case of hexahydrophenyl semicarbazide do not give the corresponding carbazides.

Hexahydrophenyl Urazole, or 3,5-Dihydroxy-1-Hexahydrophenyl Triazole.—The urazole is readily soluble in hot water and crystallizes on cooling in characteristic, thin, prismatic plates which melt at 271°. It is readily soluble in alcohol and sparingly soluble in the other common organic solvents. It does not give a color reaction with ferric chloride, shows an acid reaction to litmus, and acts as a strong reducing agent.

Analyses. Calc. for  $C_8H_{18}O_2N_3$ : C, 52.46; H, 7.10; N, 22.95. Found: C, 52.71; H, 7.25; N, 23.12.

The urazole is obtained in a yield of 74.5% by heating hexahydrophenyl semicarbazide and urea in molecular proportions. The mixture in a glycerol bath at 200° quickly liquefies with vigorous evolution of gas with the melt at a temperature of 150°. After 10 minutes the melt at a temperature of 190° becomes solid only to liquefy again after a few minutes. Toward the end of the operation, which consumes ½ hour in all, the reaction mixture again becomes solid. During the entire operation the mixture is stirred. The urazole prepared in this way acquires its ready solubility in hot water only after it has been dissolved in ammonium hydroxide and reprecipitated with acetic acid. The above method of preparing urazoles was originally used by Pinner⁹ in the preparation of the corresponding phenyl urazole from phenyl semicarbazide.

Dihexahydrophenyl Urazine or 3,6-Dihydroxy-1,4-dihexahydrophenyl-1,2,4,5-Tetrazine.—The urazine is very soluble in chloroform or alcohol, more difficultly soluble

⁹ Ref. 1, p. 1220.

in water, acetic ether, or benzene, and very difficultly soluble in ether. It can be recrystallized from acetic ether in the form of a network of fine needles, or from alcohol in slender prisms, which begin to soften at 187° and melt at 197°. Compared with the corresponding urazole, the urazine is less soluble in water and alcohol and more soluble in chloroform, benzene, and acetic ether. It acts as a strong reducing agent and gives no color reaction with ferric chloride.

Analyses. Calc. for  $C_{14}H_{24}O_2N_4$ : C, 60.00; H, 8.57; N, 20.00. Found: C, 60.32; H, 8.81; N, 20.03.

Dihexahydrophenyl carbazide and urea, heated in molecular proportions at 180° for 30 minutes, do not yield urazine, at least not in an amount sufficient for identification. This is in conformity with the structural formulas assigned here.

The most satisfactory method of preparing dihexahydrophenyl urazine is through the decomposition of the hydrochloride of the corresponding semicarbazide. When this salt is heated for  $^{1}/_{2}$  hour at 200–210°, there is very little evolution of gas and the product without liquefying becomes viscous. For isolation of the urazine, the ammonium chloride, along with a small amount of carbazide, is leached out with boiling water, the residue dissolved in ammonium hydroxide, the solution filtered from tarry matter, and the urazine precipitated with acetic acid. This method of preparation gives a 70% yield of urazine.

The Gaseous Products Evolved on Heating Phenyl Semicarbazide.—As stated above, Pinner found among the decomposition products of phenyl semicarbazide, ammonia, carbon dioxide and carbon monoxide. In testing for carbon dioxide, it should be observed that this combines with the ammonia given off to form ammonium carbamate. To determine whether carbon monoxide is formed in the decomposition of the semicarbazide, 5 g. was heated at 109° for 5 hours in an atmosphere of carbon dioxide. The gas, collected in the usual way over 30% sodium hydroxide, measured 21.5 cc. at 26° and 746 mm. No reduction of this volume was effected by scrubbing the gas with cuprous chloride, which proves quite conclusively that nitrogen and not carbon monoxide was the gas under investigation.

# Summary

- 1. Diphenyl carbazide is formed together with phenyl urazole and diphenyl urazine when phenyl semicarbazide is heated. The carbazide was identified by its characteristic color reactions.
- 2. Hexahydrophenyl semicarbazide, like phenyl semicarbazide, decomposes when heated with the formation of the corresponding carbazide, urazole and urazine. These were all isolated and analyzed.
- 3. Special methods are given in each case for the preparation in good yields of hexahydrophenyl urazole, dihexahydrophenyl carbazide and dihexahydrophenyl urazine from hexahydrophenyl semicarbazide.

AUSTIN, TEXAS

$$RAs(ONa)_2 + CICH_2COONa \longrightarrow RAs = O + NaCl^9$$
 (4)

led to the supposition that it would react with sodium arsenite as well. It has now been found that sodium chloro-acetate can be converted quantitatively into arsono-acetic acid merely by allowing it to react in aqueous solution for two hours with a 100% excess of sodium arsenite. On account of the extreme solubility of the product, it is best isolated as the barium salt.

To prepare arseno-acetic acid, barium arsono-acetate is stirred with hot aqueous sodium sulfate, barium sulfate filtered off, and the cold filtrate treated with sulfuric acid and sodium hypophosphite. On long standing in the cold there results an excellent yield of arseno compound. If the reaction mixture is heated even at a temperature as low as 50°, there is decomposition with formation of inorganic arsenic and the product is badly contaminated with polyarsenide as a result. When pure, arseno-acetic acid consists of yellow needles, which decompose above 200° without melting, and are insoluble in water and common organic solvents, but readily soluble in pyridine and in dilute aqueous alkali hydroxides and carbonates.

Aromatic polyarsenides have been prepared by the simultaneous reduction of aromatic arsonic acids and arsenious acid. ¹⁰ In a similar manner reduction of one molecular equivalent of arsenic trioxide and two of arsonoacetic acid leads to the formation of the bright vermilion-red polyarsenide, tetra-arseno-acetic acid:

OAs 
$$H_2O_3As \cdot CH_2 \cdot COOH$$
 As=As·CH₂·COOH  
OAs  $H_2O_3As \cdot CH_2 \cdot COOH$   $+ 7 H_3PO_2 \rightarrow \Big|$   $+ 7 H_3PO_3 + 2 H_2O$  (5)  
OAs  $H_2O_3As \cdot CH_2 \cdot COOH$ 

In solubility and in behavior toward heat this compound closely resembles arseno-acetic acid.

The sodium salts of arseno-acetic and tetra-arseno-acetic acids are precipitated from aqueous solution by addition of alcohol. Pharmacological tests on these salts are being performed by Professor H. G. Barbour of the University of Louisville, who will publish the results elsewhere.

The preparation of homologs and derivatives of the substances described in this communication, including aliphatic-aromatic arseno compounds, is now in progress. A similar series derived from the chlorohydrins will also be made.

⁹ Ref. 8, p. 925. Bertheim, *Ber.*, 48, 350 (1915). Ref. 2 p. Lewis and Cheetham, This Journal, 45, 514 (1923).

¹⁰ German pat., 270,254. Fargher, J. Chem. Soc., 117, 865 (1920). Christiansen, This Journal, 43, 373 (1921); 45, 1807, 2182 (1923).

# Experimental Part

Arsono-acetic Acid, ¹¹ H₂O₃As CH₂ COOH.—The second reference contains a description of the preparation of arsono-acetic acid from sodium arsenite and sodium chloro-acetate. Using the reagents in the proportion stated in this patent only one-third of the chloro-acetic acid and one-half of the arsenic trioxide are converted into calcium arsono-acetate. The melting point of the free acid is given as 152°, and of the ethyl ester as 94–95°.

The author of the present paper performed his original experiment with sodium arsenite and sodium chloro-acetate in September, 1920, and this method of synthesis was indicated in an application filed with the Research Fellowship Board, National Research Council, in February, 1921.

A solution of 99 g. of arsenic trioxide and 160 g. of sodium hydroxide in 300 cc. of water is cooled to room temperature; of this a lcc. portion is then titrated with iodine according to the common volumetric method for the determination of arsenic. In the sodium arsenite solution is dissolved 47.25 g. of chloro-acetic acid (50% of the calculated quantity) and the strongly exothermic reaction begins. At the end of two hours a second lcc. portion of the reaction mixture is removed and titrated. The result indicates that approximately one-half of the sodium arsenite has disappeared. The solution is acidified with glacial acetic acid, avoiding an excess, and cooled. Most of the remaining arsenic trioxide precipitates and is filtered off. The filtrate is poured into a solution containing 185 g. of crystallized barium chloride in 500 cc. of warm water. Barium arsono-acetate, Ba(OOC.CH₂.AsO₃Ba)₂.6¹/₂H₂O, immediately forms as a white, finely divided precipitate. It is filtered on a 15cm. Büchner funnel, washed thoroughly with water and dried on plates. The precipitated product is quite pure, but it can be recrystallized from a large volume of boiling water, in which it is sparingly soluble, as fine, feathery, colorless needles. The yield is almost quantitative (between 220 and 230 g.).

Analyses. Subs., 0.1542, 0.3587: loss at  $110^{\circ}$ , 0.0203, 0.0464. Calc. for  $C_4H_4O_{16}-As_2Ba_5.6^{1}/_2H_2O$ :  $H_2O$ , 13.13. Found: 13.16, 12.93.

Dried subs., 0.2789, 0.1410: 18.5, 9.3 cc. iodine (1 cc. = 0.00293 g. As). Dried subs., 0.2151, 0.3594: BaSO₄, 0.1922, 0.3226. Calc. for  $C_4H_4O_{10}As_2Ba_3$ : As, 19.38; Ba, 53.23. Found: As, 19.43, 19.32; Ba, 52.59, 52.82.

The necessity for using an excess of sodium arsenite is shown by an experiment with reagents as indicated theoretically in Equation 1. After the reaction mixture had stood for 4 hours it was demonstrated by iodine titration that 49% of the original sodium arsenite remained. No change was produced by 18 hours' refluxing. At this point one additional molecular equivalent of chloro-acetic acid and of sodium hydroxide were dissolved in the solution. After 4 additional hours of refluxing, 46% of the sodium arsenite had still failed to react.

Sodium arsono-acetate is prepared by adding 89.1 g. of barium arsono-acetate to a solution of 42.5 g. of anhydrous sodium sulfate in 200 cc. of hot water. The mixture is digested for 1 hour at 100° and frequently stirred. The barium sulfate is then filtered off and the filtrate concentrated on the steam-bath. Sodium arsono-acetate is obtained in several fractions having a combined weight of 47.8 g. (calc., 50.0 g.). This product contains a slight impurity of sodium sulfate, from which it is completely freed by one or two recrystallizations. In final form sodium arsono-acetate is a white, microcrystalline

¹¹ Ref. 8. Huisman, Callsen and Grüttefien, U. S. pat. 1,445,685, Feb. 20, 1923;
C. A., 17, 1534 (1923); Austrian pat. 93,325; Swiss pat. 97,977; Chem. Zenir., 1923,
IV. 721.

powder that readily dissolves in cold water to give a solution which reacts alkaline to litmus.

Analyses. Subs., 0.5544: loss at 110°, 0.0000. Subs., 0.1913, 0.1389: 19.3, 14.0 cc. iodine (1 cc. = 0.00293 g. As). Subs., 0.1729, 0.1729: Na₂SO₄, 0.1455, 0.1491. Calc. for C₂H₂O₅AsNa₃: As, 30.00; Na, 27.60. Found: As, 29.56, 29.53; Na, 27.24, 27.92.

Isolation of free arsono-acetic acid from the original reaction mixture after precipitation of the excess of arsenic trioxide is not very satisfactory, since the acid is separated from the various inorganic by-products of the reaction only by a long and inefficient process of fractional crystallization in which the solvent is gradually changed from water to alcohol. The acid is more readily obtained from the barium salt. A mixture of 22.5 g. of powdered barium arsono-acetate and 100 cc. of water containing 5 cc. of sulfuric acid (d., 1.84) is mechanically stirred at room temperature for several hours. Barium sulfate is removed by filtration and the filtrate concentrated in a vacuum over sulfuric acid in the cold. At very small volume crystallization commences. Twentyfive cc. of absolute alcohol is stirred with the mixture of crystals and viscous liquor and the insoluble, inorganic, arsenic containing material filtered off. To the filtrate 25 cc. of ligroin is added and the mixture concentrated at room temperature as before. Arsono-acetic acid now crystallizes, is filtered off, washed with ligroin and dried on a tile. The product consists of colorless, shining plates; m. p., 152° (loss of gas). It is very soluble in water and alcohol, sparingly soluble in hot glacial acetic acid, practically insoluble in ligroin, benzene, acetone, chloroform or ethyl acetate.

Analyses. Subs., 0.1778, 0.1475: 24.5, 20.3 cc. iodine (1 cc. = 0.00293 g. As). Calc. for  $C_2H_5O_5As$ : As, 40.76. Found: 40.37, 40.32.

Heating during the preparation of arsono-acetic acid as outlined above is inadvisable. Apparently the arsono group is split off very easily when arsono-acetic acid is in hot mineral acid solution and, unless heating is avoided, the isolation of the acid becomes difficult or impossible.

Arseno-acetic Acid, HOOC·CH₂·As=As·CH₂·COOH.—A solution of 12.5 g. of sodium arsono-acetate and 30 g. of sodium hypophosphite (NaH₂PO₂·H₂O) in 150 cc. of 15% sulfuric acid is allowed to stand in the cold. After two days the yellow precipitate is filtered off, washed several times with water and dried in a vacuum over sulfuric acid. When dried in air the product darkens slightly, due undoubtedly to oxidation. The filtrate is allowed to stand as before and, after two additional two-day periods, the reaction is practically complete; total yield, 6.2 g. (calc., 6.7 g.). Arseno-acetic acid forms minute yellow needles which begin to decompose at about 205°, but do not melt below 260°. It is insoluble in water and common organic solvents, but readily soluble in pyridine, dil. sodium hydroxide, and dil. sodium carbonate solutions. Usually at least one of the fractions will be found to be analytically pure and the rest nearly so.

Analyses. Subs., 0.1023, 0.1444: 19.5, 27.5 cc. iodine (1 cc. = 0.00293 g. As). Calc. for  $C_4H_6O_4As_2$ : As, 55.96. Found: 55.86, 55.80.

For the preparation of arseno-acetic acid on a larger scale it is convenient to warm the wet, freshly filtered barium arsono-acetate prepared as described above with sodium sulfate solution and to treat the filtrate from barium sulfate with sulfuric acid and sodium hypophosphite in the cold. Yields of 80–90% calculated from the chloro-acetic acid are obtained. In one run the reaction mixture was heated at 50–55° and the reduction completed in 8 hours. The orange-colored product was found to contain over 70% of arsenic. Evidently the decomposition already noted had taken place and simultaneous reduction of the arsonic acid with an inorganic arsenic compound gave a mixture composed principally of polyarsenide. In the cold this formation of inorganic arsenic is

largely prevented, but even at this low temperature later fractions of material may contain a small quantity of tetra-arseno-acetic acid.

A solution of 3.35 g. of arseno-acetic acid in 25 cc. of 5% sodium hydroxide is filtered and 75 cc. of 95% alcohol added. A yellow oil precipitates which, after several hours' standing, crystallizes in rosets composed of very fine needles. These are filtered off, washed repeatedly with 95% alcohol and dried in a vacuum over sulfuric acid; weight, 3.7 g. The salt is then in the form of a light yellow-brown powder which retains some solvent, probably alcohol, and must be dried to constant weight at  $110^\circ$  before analysis. Disodium arseno-acetate is readily soluble in water, giving a clear yellow solution which reacts slightly alkaline to litmus.

Analyses. Subs., 0.1257, 0.2081: 20.5, 34.0 cc. iodine (1 cc. = 0.00293 g. As). Subs., 0.1665, 0.2201: Na₂SO₄, 0.0768, 0.1045. Calc. for C₄H₄O₄As₂Na₂: As, 48.08, Na, 14.74. Found: As, 47.78, 47.87; Na, 14.93, 15.37.

Tetra-arseno-acetic Acid, HOOC·CH₂·As=As-As=As·CH₂·COOH,—Arsonoacetic acid is prepared from sodium arsenite and sodium chloro-acetate in a run just half the size of that described above. As soon as the reaction is complete, 150 g. of sulfuric acid (d., 1.84) and 100 g. of sodium hypophosphite are dissolved in the solution. After three hours a mixture of arsenic trioxide and sodium sulfate containing a little highlycolored organic arsenic compound is filtered off, and the filtrate is allowed to stand in the cold. A bright red precipitate gradually forms, which is filtered off at 3- to 4-day intervals, washed several times with water and dried in a vacuum over sulfuric acid. Drying in air causes the exposed surface to blacken. Altogether, five fractions are obtained, most of which are fairly pure; total yield, 25.6 g. Heating increases the rate of reaction but tends to produce an impure product. Tetra-arseno-acetic acid is a bright vermilion-red, microcrystalline powder, which begins to decompose at about 180°, but does not melt below 250°. The solubilities are closely similar to those of arseno-acetic acid.

Analyses. Subs., 0.1360, 0.1926: 33.1, 46.9 cc. iodine (1 cc. = 0.00293 g. As). Calc. for  $C_4H_6O_4As_4$ : As, 71.77. Found: 71.31, 71.37.

Seven g. of tetra-arseno-acetic acid is dissolved in 50 cc. of 5% sodium hydroxide solution. On addition of 50 cc. of 95% alcohol, a thick, dark oil is precipitated. The dilute alcohol is decanted, the residue redissolved in 50 cc. of water and an equal volume of 95% alcohol added. The precipitate can now usually be obtained crystalline. It is filtered off, washed with 50% alcohol and dried in a vacuum over sulfuric acid; weight, 6.4 g. Monosodium tetra-arseno-acetate is a red-brown powder which is considerably less soluble in water than disodium arseno-acetate. The solution is dark colored and reacts practically neutral to litmus, with possibly a slight tendency toward alkalinity. It is noteworthy that a monosodium salt is formed in spite of use of an excess of sodium hydroxide.

Analyses. Subs., 0.1090, 0.1232: 25.4, 28.8 cc. iodine (1 cc. = 0.00293 g. As). Subs., 0.1784, 0.1578: Na₂SO₄, 0.0312, 0.0286. Calc. for C₄H₅O₄As₄Na: As, 68.18; Na, 5.23. Found: As, 68.28, 68.49; Na, 5.66, 5.87.

# Summary

- 1. Action of a 100% excess of sodium arsenite on sodium chloro-acetate gives a quantitative yield of arsono-acetic acid.
- 2. Reduction of arsono-acetic acid with hypophosphorous acid produces arseno-acetic acid.
  - 3. By simultaneous reduction of one molecular equivalent of arsenic

trioxide and two of arsono-acetic acid the polyarsenide, tetra-arseno-acetic acid. is obtained.

- 4. Water-soluble sodium salts of the above acids are readily prepared.
- 5. Analogous series derived from various halogen acids and halohydrins are now being synthesized in this Laboratory.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# THE USE OF PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. IV. REDUCTION OF FURFURAL AND ITS DERIVATIVES:

By W. E. Kaufmann² with Roger Adams Received August 15, 1923

The commercial development of furfural during recent years and its remarkable cheapness has led to many investigations for new uses. This communication describes the results obtained on the catalytic reduction of furfural and a number of its simple derivatives. The reduction is of interest not only because the products might be of practical importance, but also because there has been very little work done on the reduction of compounds of the furane series. Moreover, furfural itself is a different type of aldehyde from those which have thus far been reduced with the use of platinum oxide³ as a catalyst and ferrous chloride as an activating agent.

The first work on the reduction of furfural was published in 1906 by Padoa and Ponti⁴ who passed the vapors of furfural with hydrogen over a nickel catalyst at 190°. The primary product of the reduction was furyl alcohol. Further reduction always took place and from the mixture of reaction products it was possible to isolate methyl-2-furane, methyl-2-tetrahydrofurane and pentanol-2. It may thus be seen that rupture of the ring took place during reduction, though to only a very slight extent. The same authors reported that when they used a temperature of 270° the decomposition yielded in addition furane and carbon monoxide.

Law⁵ studied the electrolytic reduction of furfural in the presence of alkali and acid but, with the exception of a small amount of furyl alcohol when the acid solution was used, only resins were obtained.

Pringsheim and Noth⁶ reduced furfural by passing the vapors with hydrogen over

¹ Part of the chloroplatinic acid used in this investigation was purchased with the aid of a grant from the Bache Fund of the National Academy of Sciences. For this aid the authors are greatly indebted.

² This communication is an abstract of a thesis submitted by W. E. Kaufmann in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

³ (a) Voorhees and Adams, This Journal, 44, 1397 (1922). (b) Carothers and Adams, 45, 1071 (1923). (c) Adams and Shriner, 45, 2171 (1923).

⁴ Padoa and Ponti, Atti. R. accad. Lincei, 15, [5] 610 (1906); Gazz. chim. ital., 37, [2] 105 (1907).

⁵ Law, J. Chem. Soc., 89, 1517 (1906).

⁶ Pringsheim and Noth, Ber., 53, 114 (1920).

iron as a catalyst at 200°. They observed the formation of the same products reported by Padoa and Ponti when nickel was used and in addition, furane and dihydrofurane. They concluded that in the reduction of furfural (1) the aldehyde group can be reduced to a methyl, (2) the aldehyde group may be eliminated entirely with the formation of furane or hydrogenated furanes, and finally (3) the ring is ruptured and the resulting products are hydrogenated.

More recently, the reduction of furfural has been undertaken by Wienhaus, using charcoal impregnated with palladium chloride solution as a catalyst and reducing with hydrogen at ordinary temperatures and one atmosphere pressure. The reduction was carried out in the presence of water as well as without any solvent. There was thus obtained as a chief product tetrahydrofuryl alcohol, but in addition high-boiling products which the author supposed to be bimolecular compounds similar to those reported by Skita in the reduction of citral. These, however, were not investigated. The reaction was apparently quite unsatisfactory since it required 285 hours' time with 10 additions of fresh catalyst for the reduction of 48 g. of furfural. By the reduction of furyl alcohol the same author obtained a reaction mixture similar to that from furfural itself, thus indicating that furyl alcohol was the primary reduction product.

The reduction of furane and other derivatives besides furfural has been less extensively studied. Bourgignon's reported the reduction of furane with hydrogen and a nickel catalyst at 170°. A large portion of the furane was recovered unchanged and, in addition, a small amount of tetrahydrofurane and n-butyl alcohol.

Douris's reduced furyl ethyl carbinol with hydrogen and nickel catalyst at 175° and obtained as the chief product ethyl tetrahydrofuryl carbinol. As by-products were formed propyl-2-tetrahydrofurane, propyl-butyl ether, propyl-butadienyl ether, dipropyl ketone and a sirup which was not purified but which the author believed to be a glycol.

Yoder and Tollens¹⁰ showed that by the action of sodium amalgam, pyromucic acid was not reduced. On the other hand, with this same reagent Hill and Wheeler¹¹ reduced furane-2,5-dicarboxylic acid readily to the tetrahydro derivative.

 $\beta\textsc{-Furyl-acrylic}$  acid has been reduced by Markwald with phosphorus and hydriodic acid to pimelic acid.  12 

Semler¹³ reduced fural-acetophenone with sodium and alcohol to furyl-phenyl-propane. Apparently no reduction of the furane ring took place in this reaction.

Catalytic reduction with platinum or palladium catalyst has been used on a number of furfural derivatives. Wienhaus and Sorge¹⁴ reduced pyromucic acid in the presence of platinum chloride and gum arabic to a product which they identified as tetrahydropyromucic acid. The reduction, just as with furfural itself, took place only very slowly and no yield was reported. Asahina and Shibata, ¹⁵ by means of hydrogen and platinum black in acetic acid, reduced methyl  $\beta$ -furyl-propionate to methyl  $\beta$ -tetrahydrofuryl-propionate. Windaus and Dalmer, ¹⁶ using hydrogen and platinum black, reduced  $\beta$ -furyl acrylic acid to  $\beta$ -tetrahydrofuryl-propionic acid. Finally, Bargellini and Marte-

⁷ Wienhaus, Ber., 53, 1656 (1920).

⁸ Bourgignon, Bull. soc. chim. Belg., 22, 87 (1908).

Douris, Compt. rend., 157, 722 (1913).

¹⁰ Yoder and Tollens, Ber., 34, 3462 (1901).

¹¹ Hill and Wheeler, Am. Chem. J., 25, 463 (1901).

¹² Markwald, Ber., 21, 1401 (1888).

¹³ Semler, Ber., 39, 726 (1906).

¹⁴ Wienhaus and Sorge, Ber., 46, 1927 (1913).

¹⁵ Asahina and Shibata, J. Pharm. Soc. Japan, 423, 391, 400 (1917).

¹⁶ Windaus and Dalmer, Ber., 53, 2304 (1920).

giani¹⁷ reduced fural-acetophenone with hydrogen and platinum or palladium black. They reported that only the ethylene double bond in the side chain was hydrogenated. Since quite different results were obtained in this investigation it may be mentioned that the method of these authors consisted merely in bubbling the hydrogen through a warm solution of the substance in alcohol without using pressure.

In this investigation the reduction of furfural, fural-acetone, fural-acetophenone, furoin, pyromucic acid, ethyl pyromucate and  $\beta$ -furyl-acrylic acid was studied. Alcohol was used as a solvent, and the catalyst employed was the platinum oxide³ recently described and shown to be so active for the reduction of various types of organic compounds.

No difficulty was observed in the reduction of furfural when the proper conditions were used. The first experiments in this investigation consisted in determining the nature of the product obtained by the absorption of 1 molecular equivalent of hydrogen. It was found that a quantitative yield of furyl alcohol resulted, thus establishing without question that the initial point of attack of the hydrogen was the aldehyde group and that no other part of the molecule reacted until after the aldehyde group was completely reduced.

The other experiments were carried out to determine the nature of the products of reduction when as much hydrogen was absorbed as would be taken up. Instead of the absorption of three molecular equivalents of hydrogen, as would be expected if merely the aldehyde and the two double bonds of the furane ring were reduced, it was always found that more was absorbed, 3.2 to 4.3 molecular equivalents, the amount depending generally upon the type of catalyst used, the mode of reactivation and the length of time the reactions were allowed to proceed at the very end of the absorption. The reaction mixture obtained by the complete reduction of 12 runs of 50 g. each of furfural was worked up at one time. After distillation of the alcohol a brown oil resulted which weighed approximately 600 g., showing that no very volatile materials had been produced. The mixture was first carefully fractionated a number of times under diminished pressure until it separated into four main fractions, each boiling within a few degrees. These fractions were then redistilled independently and constant boiling products isolated. The first substance boiled at 137-139° at 751 mm. and proved by analysis and by its physical constants to be n-amyl alcohol. The second substance boiled at 176-177° at 751 mm. and was pure tetrahydrofuryl alcohol. Its constants agreed exactly with those described in the literature for this substance. The third substance boiled at 210.5-211.5° at 751 mm. By analysis and its formation of a diacetate it was shown to be a pentane glycol. It undoubtedly was pentanediol-1,2, a substance which has not been previously described. The fourth substance boiled at 239-241° at 751 mm. and was shown to be pentanediol-1,5. By analysis and by a comparison of its physical constants and those of its diacetate with

17 Bargellini and Martegiani, Gazz. chim. ital., 42, [2] 417, 427 (1912).

the constants given in the literature for these substances, the compound was identified. Practically no residue was obtained. The four main fractions, from the lowest to the highest boiling weighed, respectively, 60 g., 222 g., 131 g. and 51 g. These figures do not represent the weight of pure materials obtained, but give some idea of the approximate proportion of each compound present in the mixture for one set of runs. The mechanism for the formation of these various products is best illustrated in the following chart.

Since the first molecular equivalent of hydrogen absorbed by the furfural gave a quantitative yield of furyl alcohol (I), it is obvious that the reduction of furyl alcohol itself must take place in a number of different ways. The main reaction is obviously simple hydrogenation of the double bonds in the furane ring with the formation of the tetrahydrofuryl alcohol (II). On the other hand, part of the reduction takes place between the oxygen of the furane and one or the other of the two carbons to which it is attached. By

the reduction at Point A in Formula I, an intermediate substance is obtained which would immediately be reduced to pentanediol-1,2 (III). If the reduction took place at Point B in Formula I, an intermediate product would be formed which would reduce immediately to pentanediol-1,5 (IV). The *n*-amyl alcohol (V) may be formed either by the subsequent reduction of one of the glycols, possibly the pentanediol-1,2 or more probably by the direct reduction and elimination of oxygen from the furane ring of the furyl alcohol with immediate reduction of the intermediate product. The formation of the glycols or *n*-amyl alcohol certainly does not take place through the tetrahydrofuryl alcohol as an intermediate, since pure tetrahydrofuryl alcohol could not be reduced to the slightest extent under the conditions used for the reduction of furfural.

A comparison of the rupture of the furane ring by this reduction method and those previously employed is of interest. The opening of the furane

ring at ordinary temperatures, as found in this investigation, is apparently much greater in amount than that which takes place by the use of other catalytic methods where high temperatures are employed. Moreover, the high temperature catalytic reductions gave a larger number of products and the number apparently varied with slight changes in conditions. Only the same four products of reaction were ever obtained in this work.

The character of the catalyst had a marked effect upon the speed of the reduction of the furfural. The results of the different experiments were of such general interest that a detailed discussion of the catalyst is necessary. In the previous paper it was shown that the platinum oxide made from spectroscopically pure chloroplatinic acid was a very inefficient catalyst toward the reduction of benzaldehyde. This same thing has been observed in the reduction of furfural; only by reactivation of the catalyst could the reduction be carried out at all, and then only very slowly. The presence of small amounts of ferrous chloride, however, caused the same marked increase in the activity of the catalyst as was shown in the case of benzaldehyde and heptaldehyde. In standard experiments on the reduction of these latter compounds, an increase in the amount of ferrous chloride, without changing the quantities of the other reagents, had practically no effect upon the speed of reduction after a certain minimum quantity had been added. In the reduction of furfural, however, this was not the case. With increasing amounts of ferrous chloride the speed of reduction increased to a point beyond which it decreased rapidly. No explanation of this fact has yet been found and a further study of the effect of ferrous chloride is necessary.

In the experiments to determine these facts, 25 g. of furfural, 75 cc. of alcohol and 0.5 g. of catalyst (sp. p.)18 were used with various quantities of ferrous chloride. The most effective amount tried was 1.2 cc. of 0.1 M ferrous chloride. The results obtained using twice these amounts of reagents, namely 50 g. of furfural, 150 cc. of alcohol and 1 g. of platinum oxide with various amounts of ferrous chloride, were surprising. It was expected that for such a run as this, 2.4 cc. of 0.1 M ferrous chloride would activate the platinum so as to cause the reduction of this larger quantity to take place with the same speed as shown in the smaller run. This, however, was not the case. With 2.4 cc. of ferrous chloride, the reduction of the furfural did not take place as rapidly as in the smaller runs. On the other hand, if only 1.2 cc. of ferrous chloride was used, the same as in the smaller runs, the reduction proceeded just as rapidly. These results indicate that a certain amount of ferrous chloride can just as effectively activate small or large amounts of platinum catalyst. Further study of this relationship with other aldehydes is being made.

With these data available, it is not surprising that in a series of runs of

^{18 &}quot;Sp. p." is an abbreviation indicating that the catalyst was prepared from spectroscopically pure chloroplatinic acid.

25 g. of furfural, 75 cc. of alcohol, 0.5 g. of catalyst (sp. p.) and 1.2 cc. of 0.1 M ferrous chloride, it was found that when, after complete reduction of the furfural, the liquid was decanted and fresh quantities of furfural and alcohol were added, the addition of more ferrous chloride in the second run was unnecessary. In fact, when ferrous chloride was added, the reduction of the second portion of aldehyde was slower than the reduction of the first; without addition of ferrous chloride to the second run, the reduction was just as rapid as in the first run. The same conditions held true with the third run, using the same platinum catalyst. When ferrous chloride was added in the first run, also in the second and still again in the third, the reduction was much slower in the third than in the second run and it was quite obvious that the catalyst was being gradually rendered ineffective by further additions of ferrous chloride. On the other hand, with no further addition of ferrous chloride after the first run, the platinum catalyst proved to be practically as effective in the second, third, fourth and fifth runs. In all these experiments the amount of activity restored to the catalyst after reactivation with air or oxygen was proportional to that activity held initially by the catalyst in the presence of any given quantity of ferrous chlorahi

It is noticeable that in these series of reductions where further addition of ferrous chloride tended to cause a diminution in the speed of reduction, the diminution in speed of absorption of the first two hydrogens to reduce the aldehyde group was much less than the diminution in speed of absorption of the succeeding two to three molecular equivalents of hydrogen. The larger amount of ferrous chloride, at the same time as it acts as a protection for the platinum catalyst from de-oxygenation, poisons the catalyst more readily in its activity toward the reduction of the ethylene double bonds than it does toward the reduction of the aldehyde group.

From these results it may be concluded that in the reduction of furfural, as soon as a sufficient amount of ferrous chloride has been added to activate the platinum catalyst, no more is necessary and this catalyst then remains exceedingly active in the reduction experiments, only an occasional reactivation with air or oxygen being necessary in order to reduce run after run of furfural without changing the catalyst. No attempt was made to find out how many portions of furfural could be reduced with the same catalyst under the conditions mentioned before the catalyst might become appreciably affected.

Many of the experiments in this investigation were carried out with platinum catalyst prepared from spectroscopically pure chloroplatinic acid. For the average laboratory, it would be a tedious matter to bring all the platinum to this state of purity before using it. Experiments were, therefore, conducted to determine whether similar results to those described above could not be obtained by using platinum oxide from the c. p. chloro-

platinic acid of commerce. Such platinum oxide, without the addition of ferrous chloride, proved to be a more effective catalyst in the reduction of furfural than the oxide from spectroscopically pure chloroplatinic acid but the activity did not approach that obtained when a little ferrous chloride was present. The difference in the activity of the oxide from the two grades of chloroplatinic acid may be attributed to the presence of traces of iron or other effective impurities in the c. p. chloroplatinic acid of commerce. The results of several experiments show that by the addition of the proper amount of ferrous chloride to the platinum oxide from c. p. chloroplatinic acid of commerce, results could be obtained almost identical with those described by the use of platinum oxide from purest raw material.

It was pointed out in previous papers that the catalyst from the c. p. chloroplatinic acid of commerce, after it had been reworked 19 several times, gradually accumulated sufficient impurities so that it became quite active as a catalyst in the reduction of aldehydes without the necessity of adding ferrous chloride. Moreover, the effectiveness of such a catalyst obtained by frequent reworking remained constant after a maximum activity had been reached. Such a catalyst was used for the reduction of a large amount of furfural. Using 50 g. of furfural, 150 cc. of alcohol and 1 g. of such platinum oxide, it was possible to complete the reduction (3.3 to 3.6 molecular equivalents) within a reasonable time with about six reactivations of the catalyst with air with each 50 g. of furfural. As many as six successive runs of 50 g. each of furfural were made with the same catalyst and only a slight diminution in the speed of reduction was noted. The speed of this reduction was less than half that which was obtained by the use of platinum oxide with the addition of the proper amount of ferrous chloride. Although no similar experiments were carried out with this catalyst in which oxygen was used for reactivation, it is probable that the time of reduction could be cut in half by such a procedure, as indicated by the results discussed in the following paragraph.

The importance and usefulness of reactivating the platinum catalyst during reduction experiments have been emphasized by a number of investigators, as well as in the previous papers on the use of platinum oxide as a catalyst. The procedure, as usually carrried out, is merely to shake the catalyst with air for a few minutes. The advantage of using oxygen in place of air for the reactivation has not been sufficiently emphasized. Standard experiments with exactly the same quantities of reagents were carried out, the only difference being in the mode of reactivation of the catalyst. By the use of oxygen, the time for reduction was much less than when air was used.

¹⁸ The term "reworked" has been applied to that platinum oxide which was made from chloroplatinic acid formed after a number of cycles as follows: chloroplatinic acid to platinum black→use of the platinum black as a catalyst→solution of the platinum black to give chloroplatinic acid.

From the variety of reduction experiments which have been completed, the best results were obtained as follows. A mixture of 50 g. of furfural in 150 cc. of alcohol, 1 g. of catalyst (either from c. p. or sp. p. chloroplatinic acid) and 1.2 cc. of 0.1 M ferrous chloride was treated with hydrogen under 1 to 2 atmospheres' pressure (Table I). One molecular equivalent of hydrogen was absorbed in about an hour, and the reduction ran to completion with the absorption of about 3.3 to 4.3 molecular equivalents of hydrogen in about 4 hours. During the reduction the catalyst was thrice reactivated with oxygen. When the reduction was complete the solution was decanted from the platinum, the catalyst reactivated with oxygen and then 50 g. of furfural in 150 cc. of alcohol was added. The reduction proceeded in practically the same time as for the first 50 g. A third run was carried out in a similar manner and gave the same results without showing any appreciable devitalization of the catalyst. Unquestionably, still additional portions of 50 g. of furfural could have been reduced with the same catalyst without appreciable diminution in the speed of reduction.

Furfural is a different type of aldehyde than those studied in a previous paper by Carothers and Adams, in that it contains additional reducible groups. In the reduction of furfural a difference in the speed of absorption of the first molecular equivalent of hydrogen to convert the aldehyde group to the alcohol was observed as compared with the reduction of the ethylene double bonds in the furane ring. This was particularly noticeable in those experiments where the reduction was not too rapid, illustrated especially well in the series of runs where reworked platinum catalyst was used without the addition of ferrous chloride and where air was employed for reactivating the catalyst. The first portion of hydrogen was invariably absorbed rapidly, but usually one whole molecular equivalent was not absorbed before reactivation of the catalyst was desirable. It was especially noticeable that the last fraction of the first molecular equivalent of hydrogen was slowly absorbed, and that as soon as one molecular equivalent was completely absorbed a second reactivation was desirable. As soon as the absorption of the second molecular equivalent of hydrogen had started with the reactivated catalyst, the reduction proceeded again very rapidly. The significant point in these experiments is that just as long as any aldehyde is present the platinum catalyst is rapidly rendered inactive, but just as soon as all the aldehyde is reduced, the platinum catalyst is not devitalized and the reduction continues to proceed rapidly. It frequently happened in these experiments that after all but 5 to 10% of the first molecular equivalent of hydrogen had been absorbed, the last 5 to 10% could not be absorbed even over a long period of time, unless the catalyst was reactivated. After reactivation the absorption of this last small amount did proceed fairly rapidly, but during the process, devitalized the catalyst considerably so that reduction, after the first molecular equivalent of hydrogen had been absorbed, went more slowly than it should. When, however, the catalyst was always reactivated just after the complete absorption of the first molecular equivalent of hydrogen, regardless of when the previous reactivation had been made, the reduction of the ethylene linkages in the furane ring went very rapidly.

In all of the experiments described above no attempt was made to control the temperature. It was noted, however, that whenever the hydrogen was absorbed rapidly, there was a marked increase in the temperature of the reaction mixture. If the reduction slowed down appreciably, the reaction mixture might cool off but become warm again as soon as the platinum catalyst was reactivated. In the experiments in which the oxygen was used for reactivation and the maximum activity was obtained by using ferrous chloride, the reaction mixture remained at a temperature of  $50\text{--}60^{\circ}$  during the whole period of reduction, merely due to the heat of reaction.

A few experiments were carried out in order to determine whether furfural might be reduced without using a solvent, or using only a small amount of solvent. It was found that furfural alone with the catalyst was not reduced. Neither was it reduced in the presence of water sufficient in amount not to cause the formation of two layers. On the other hand, satisfactory results were obtained by dissolving the furfural in twice its volume of 50% alcohol. Since the preliminary experiments showed that the furfural in three volumes of 95% alcohol reduced very satisfactorily, this proportion was arbitrarily adopted.

In previous papers it has been mentioned that the brown platinum oxide could either be added to the reaction mixture and the reduction started, or the platinum oxide could first be added to the solvent, reduced to platinum black and then the reagents added and the reduction started. In all of the work with furfural the platinum oxide was reduced first to platinum black before the other reagents were added.

The reduction of furfural derivatives was carried out with platinum oxide obtained from chloroplatinic acid which had been reworked several times. The reactivation of the catalyst was carried out with air. All of the experiments were made before the study of furfural itself was completed, so that perhaps the best conditions were not used in every case. Nevertheless, the reductions took place in most cases with surprising ease. Apparently, the devitalizing of the catalyst which occurred in the reduction of furfural did not occur in the reduction of the majority of derivatives. Although the speed of reduction for each of these substances is given in the Experimental Part, it is not particularly significant, since the probability is that by varying the conditions somewhat according to those used for furfural, it could be increased markedly.

Pyromucic acid was reduced with the formation of tetrahydro-pyromucic acid as a chief product. Lower- and higher-boiling fractions were formed,

however, the contents of which have not yet been determined. From analogy to the reduction of furfural it might be concluded that these fractions contain valerianic acid,  $\alpha$ -hydroxy- and  $\delta$ -hydroxy-valerianic acids.

The reduction of ethyl pyromucate took place only very slowly with the formation of a satisfactory yield of ethyl tetrahydro-pyromucate. It was obvious that very little decomposition of the ring took place as compared with the reduction of pyromucic acid.

The reduction of  $\beta$ -furyl-acrylic acid proceeded very rapidly with the absorption of three molecular equivalents of hydrogen to form  $\beta$ -tetrahydrofuryl-propionic acid. The by-product obtained in this reaction was small in amount, indicating the probable opening of the ring to only a very slight extent.

The reduction of furoin resembled closely the reduction of furfural owing, perhaps, to its similarity to furyl alcohol, the primary product in the reduction of furfural. By the absorption of 5 molecular equivalents, two glycols were obtained which, by analysis, proved to be stereo-isomeric dihydroxy-1,2-di-(tetrahydrofuryl)-1,2-ethanes. Besides these, some oily material resulted which was probably a complex mixture of polyhydroxy compounds such as might be formed by the rupture of one or both of the furane rings. The reduction was undoubtedly not complete when the hydrogenation was stopped.

The reduction of fural-acetone and fural-acetophenone took place with exceptional smoothness. A total of 4 molecular equivalents of hydrogen were absorbed before the reduction stopped; the first three were taken up very rapidly, reducing the aliphatic double bond and the two double bonds in the furane ring in each of the substances. The fourth molecular equivalent of hydrogen was absorbed comparatively slowly. When the reaction mixture was worked up after the first 3 molecular equivalents were absorbed, practically quantitative yields of pure ketone were obtained. When, however, 4 molecular equivalents were absorbed, the corresponding alcohol was obtained in quantitative yields. It has already been mentioned by previous investigators that fural-acetophenone could be reduced by hydrogen and platinum only to the saturated ketone. This is obviously incorrect.

## Experimental Part

Materials.—The furfural used in this work was kindly donated by the Miner Laboratories of Chicago, Illinois. The authors wish to express their appreciation of this gift. The commercial material was purified merely by distillation under diminished pressure. It was then placed in brown bottles and kept until needed for use.

The pyromucic acid was prepared by the method of Frankland and Aston,  20   $\beta$ -furyl-acrylic acid by the method of Gibson and Kahnweiler,  21  furoin by the method of

²⁰ Frankland and Aston, J. Chem. Soc., 79, 515 (1901).

²¹ Gibson and Kahnweiler, Am. Chem. J., 12, 314 (1890).

Fischer, ²² fural-acetone by the method of Claisen²³ and fural-acetophenone by the method of Semler, ²⁴

The spectroscopically pure chloroplatinic acid was made from ordinary c. p. chloroplatinic acid 25  of commerce by the method of E. Wichers. 26 

Reduction Experiments.—The apparatus used in the reduction was that described previously in this series of papers.³

The platinum oxide catalyst was made from chloroplatinic acid by the method described in the last paper. In all the experiments the platinum oxide was reduced to platinum black before the substance to be reduced was added. The procedure followed in each case was to add the platinum oxide to the reaction flask and wash it in carefully with a little water. There was then added sufficient alcohol to make the liquid about a 50% alcohol and then it was shaken with hydrogen under pressure until the platinum oxide turned black. This required from half a minute to a maximum of two or three minutes, providing the platinum oxide had originally been prepared in the proper way. The 50% alcohol which was present was allowed to remain in the bottle when the solution of alcohol for reduction was added.

The reductions were all carried out with hydrogen under a pressure of 1 to 2 atmospheres.

The reactivations of the catalyst were all carried out in a similar way. The bottle was evacuated, air or oxygen was passed in and the reaction mixture shaken for 10 minutes. The bottle was then again evacuated and filled with hydrogen before the reduction was continued. The first reactivation of the catalyst was invariably carried out an hour after the start of the reduction. Subsequent reactivations were made hourly in those experiments where the reductions proceeded rapidly, or every two or more hours in those experiments where the reductions were slow.

The procedure for working up the reaction mixture was very simple. As soon as the reduction was complete the bottle was allowed to stand for perhaps 30 minutes until the platinum settled. The solution was decanted or filtered, the alcohol distilled and the resulting residue fractionated under ordinary or diminished pressure.

**Explanation of Table.**—The total molecular equivalents of hydrogen which had been absorbed after definite periods of time are given in one column. The readings that were actually taken represented fall in pressure which was then converted to molecular equivalents of hydrogen. Since

²² Fischer, Ber., 13, 1334 (1880).

²³ Claisen, Ber., 14, 2468 (1881).

²⁴ Ref. 13, p. 729.

²⁵ The C. P. chloroplatinic acid in this investigation was the C. P. grade purchased from the Mallinckrodt Chemical Company. It contained traces of iron and other impurities.

²⁶ Wichers, This Journal, 43, 1268 (1921).

the drop in pressure varied between different limits, the molecular equivalents are approximate but are all within the general experimental error.

The asterisk (*) represents reactivation with oxygen, as described above. The reactivations were made at the ends of the time periods represented by the numbers directly before the signs, and also at beginning of each successive run (B, D, E) of a series.

Ten complete tables of exact experimental results which have led to the conclusions discussed in the introductory part of this paper could not be published on account of the necessity of conserving space in This Journal. If desired, copies of these tables may be procured by writing to the author (Adams).

TABLE I
BEST CONDITIONS FOR RAPID REDUCTION OF FURPILIFAL

Columns A and B represent reduction with the same 1 g. of catalyst (c. p.), each run containing 50 g. of furfural in 150 cc. of alcohol (95%). Expts. C, D and E present a series of runs with the same 0.5 g. of catalyst (sp. p.) each run using 25 g. of furfural, in 75 cc. of alcohol (95%). To Run A only was added 1.2 cc. of 0.1 M ferrous chloride.

H	Mol. equiv. rs. H ₂	B Hrs.	Mol. equiv. H2	Hrs.	Mol. equiv. H ₂	E Hrs.	Mol. equiv.	Hrs.	Mol. equiv. H2
1	* 0.840	1*	1.04	1	1.040	1*	1.058	1*	1.058
2	* 1.380	2*	1.900	2*	2.310	2*	2.443	2*	2.173
3	2.580	3	3.060	3*	3.462	3	3.483	3	3.402
4	3.540								

Isolation of Products from Furfural Reduction.—The best results were obtained by distilling the crude material obtained from the reduction of six 50g. runs under ordinary pressure until all of the material boiling below 180° had passed over. This removed all the low-boiling products and most of the tetrahydrofuryl alcohol. The remainder was distilled under diminished pressure, and fractions were collected as follows: to 80°/3 mm., 80–95°/3 mm., 95–105°/3 mm., 105–118°/3 mm., 118–123°/3 mm. Three refractionations were then carried out under diminished pressure until most of the material had separated into fractions boiling up to 80°/3 mm., 95–105°/3 mm., and 118–123°/3 mm. These three fractions were then distilled under ordinary pressure and pure materials obtained as described below.

n-Amyl Alcohol (V).—From each 600 g. of furfural only a very small amount of the fraction boiling at 130–145° was obtained. By careful fractionation, 5 g. was isolated which boiled at 137–139° (751 mm.);  $n_1^{15}$ , 1.4114;  $d_2^{20}$ , 0.8266. It had the characteristic odor of amyl alcohol and gave the proper constants and analytical results.

Analyses. Subs., 0.2757:  $CO_2$ , 0.6872;  $H_2O$ , 0.3282. Calc. for  $C_6H_{12}O$ : C, 68.18; H, 13.63. Found: C, 67.98; H, 13.32.

Undoubtedly the amount of this product formed was considerably greater than that actually isolated in a pure state.

Tetrahydrofuryl Alcohol (II).—From the material boiling at 145-180° a large frac-

tion boiling at 174–180° was obtained which proved to be identical with the tetrahydro-furyl alcohol made and described in the literature. When pure it boiled at 177–178° (743 mm.);  $n_{\rm p}^{19}$ , 1.4502;  $d_{\rm 20}^{20}$ , 1.0514.

Pentanediol-1,2 (III).—The fraction boiling at 95–105° (3 mm.) upon fractionation under ordinary pressure gave a large proportion boiling at 210.5–211.5° (751 mm.) or 99–100° (3 mm.);  $n_{\rm p}^{19}$ , 1.4412;  $d_{\rm p}^{20}$ , 0.9802.

Analyses. Subs., 0.8086: CO₂, 0.6493;  $H_2O$ , 0.3155. Calc. for  $C_5H_{12}O_2$ : C, 57.69; H, 11.53. Found: C, 57.38; H, 11.44.

This product was further identified as a glycol by conversion into the diacetate.

Pentanediol-1,2-diacetate.—The glycol was refluxed with a large excess of acetic anhydride for 3 hours. The reaction product was then fractionated under diminished pressure and yielded a practically quantitative amount of a diacetate boiling at  $219-220^{\circ}$  (748 mm.) or  $103-104^{\circ}$  (2 mm.);  $n_{\rm p}^{20}$ , 1.4202;  $d_{\rm 20}^{20}$ , 1.0148.

Analyses. Subs., 0.3962:  $CO_2$ , 0.8341;  $H_2O$ , 0.2988. Calc. for  $C_9H_{16}O_4$ : C, 57.44; H, 8.51. Found: C, 57.42; H, 8.44.

Pentanediol-1,5; (Pentamethylene Glycol) (IV).—The high-boiling fraction of the original reaction mixture gave, upon distillation, constant-boiling fractions at 237–239° (751 mm.) or 119–120° (3 mm.);  $n_D^{20}$ , 1.4499;  $d_D^{20}$ , 0.9939. It was a practically water-clear liquid, miscible with water, alcohol and ether. Its constants agree with those of pentamethylene glycol prepared in a different manner. It gives a diacetate the constants of which agree with those previously found for this compound.

Analyses. Subs., 0.2349: CO₂, 0.4968;  $H_2O$ , 0.2383. Calc. for  $C_5H_{12}O_2$ : C, 57.69; H, 11.53. Found: C, 57.68; H, 11.36.

Pentanediol-1,5-diacetate.—This was prepared in exactly the same manner as the pentanediol-1,2-diacetate. It was a colorless liquid boiling at  $241.5-243.5^{\circ}$  (748 mm.) or  $122-123^{\circ}$  (3 mm.);  $n_D^{19}$ , 1.4261;  $d_D^{20}$ , 1.0296.

Analyses. Subs., 0.2765: CO₂, 0.5799; H₂O, 0.2099. Calc. for  $C_9H_{16}O_4$ : C, 57.44; H, 8.51. Found: C, 57.20; H, 8.50.

Furyl Alcohol (I).—From 200 g. of furfural reduced in 50 g. portions merely until one molecular equivalent of hydrogen had been absorbed, using the same 1 g. of catalyst, there was obtained 180 g. of practically pure furyl alcohol boiling at 168–170° (754 mm.);  $n_2^{20}$ , 1.4828;  $d_2^{20}$ , 1.1357.

#### Reduction of Furfural Derivatives

Catalyst (c. P.) was used in all the experiments on furfural derivatives and reactivations with air were employed. The experiments were completed before the distinct advantage of using oxygen for reactivation was found.

Pyromucic Acid to Tetrahydro-pyromucic Acid.—A sample of 25 g. of pyromucic acid in 100 cc. of alcohol (95%) was reduced with 0.5 g. of catalyst in about 4 hours. By fractionation of the reaction product tetrahydro-pyromucic acid was obtained to the extent of about 40% of the total reaction mixture. In addition, there were low- and high-boiling products present which are now being studied. Wienhaus and Sorge¹⁴ did not in their work mention that any products besides tetrahydro-pyromucic acid were obtained. When pure, tetrahydro-pyromucic acid was water-clear and boiled at  $131-132^{\circ}$  (14 mm.); m. p.,  $21^{\circ}$ ;  $n_{19}^{19}$ , 1.4585;  $d_{20}^{20}$ , 1.1933.

Ethyl Pyromucate to Ethyl Tetrahydro-pyromucate.—The reduction of ethyl pyromucate took place much more slowly than the reduction of pyromucic acid. For the reduction of 25 g. of ethyl pyromucate in 75 cc. of 95% alcohol in the presence of 0.5 g. of catalyst, 45 hours was necessary with frequent reactivation of the catalyst with air. About 20 g. of crude reduction product was obtained from the reaction mixture and

of this 13 g. boiled at a constant temperature of 82° (11 mm.);  $n_{\rm p}^{18}$ , 1.4455;  $d_{20}^{20}$ , 1.0792. It had a pleasant, fruity odor, and was insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.4049: CO₂, 0.8620; H₂O, 0.3105. Cale. for C₇H₁₂O₃: C, 58.29; H, 8.39. Found: C, 58.06; H, 8.56.

β-Furyl-acrylic Acid to β-Tetrahydrofuryl-propionic Acid,  $C_4H_7O$ — $CH_2CH_2$ - $CO_2H$ .—The reduction of 25 g. of β-furyl-acrylic acid in 75 cc. of 95% alcohol in the presence of 0.5 g. of catalyst was complete in about 2 hours. After fractionation 10 g. of pure β-tetrahydrofuryl-propionic acid was obtained boiling at 135–137° (4 mm.);  $n_p^{19}$ , 1.4562;  $d_{20}^{20}$ , 1.1155. It was obviously identical with the substance prepared by Windaus¹6 and Dalmer. In addition to this main product was low- and high-boiling material which has not yet been identified.

Furoin to Dihydroxy-1,2-di-(tetrahydrofuryl)-1,2-ethane,  $C_4H_7O$ —CHOHCH-OH— $C_4H_7O$ .—A solution of 20 g. of pure furoin in 200 cc. of 95% alcohol was reduced with 1 g. of catalyst. The initial temperature in this experiment was about 35°, since furoin is not very soluble in cold alcohol, and even at the temperature mentioned a certain amount remained undissolved. The reduction proceeded rapidly and at the end of 6 hours, the catalyst having been reactivated with air only once, five molecular equivalents of hydrogen had been taken up. Apparently, further reduction was taking place but it was stopped at this point. Two such runs as these were made and the reaction products mixed before being worked up.

After filtering the platinum and evaporating the alcohol, a liquid was obtained from which a few crystals deposited on standing. The whole mixture, without removal of these crystals, was distilled under diminished pressure, when the major portion boiled from 145-200° (2 mm.). This distillate was a yellowish oil from which crystals deposited on standing. The crystals were filtered out and recrystallized from a very small amount of 95% alcohol. About 4 g. of the recrystallized product was thus obtained (Product A). The alcoholic filtrate from the recrystallization was added to the oil from which the crude crystals had been filtered and the alcohol removed from the mixture. There resulted 34 g. of yellow oil which on standing became semisolid. This was again fractionated under diminished pressure and two portions were collected, one boiling at 140-170° at 2 mm. and the other at 170-205° at 2 mm. The higher of these two fractions gradually solidified in the receiver. It weighed about 5 g. and contained a large percentage of Product A.

The fraction boiling from 140–170° (2 mm.) and weighing 26 g. was again fractionated and a constant-boiling fraction distilling at 147–148° (2 mm.) obtained. This solidified immediately to a pure white substance which melted at 75° (Product B). About 12 g. of this solid was obtained. No convenient method for recrystallizing it was found.

PRODUCT A.—Product A is a white crystalline solid, readily soluble in water and alcohol but only slightly soluble in ether, benzene or ethyl acetate. It can readily be crystallized from alcohol after which it melts at 167°.

Analyses. Subs., 0.2687:  $CO_2$ , 0.5843;  $H_2O$ , 0.2100. Calc. for  $C_{10}H_{18}O_4$ : C, 59.36; H, 8.98. Found: C, 59.30; H, 8.75.

PRODUCT B.—Product B is a white solid readily soluble in alcohol and water. It is more soluble in benzene, ether or ethyl acetate than Product A. It boils at 147–148° (2 mm.) after which it solidifies and melts at 75°.

Analyses. Subs., 0.2782: CO₂, 0.5982;  $H_2O$ , 0.2188. Calc. for  $C_{10}H_{18}O_4$ : C, 59.36; H, 8.98. Found: C, 58.64; H, 8.80.

Fural-acetone to Tetrahydrofuryl-1-butanone-3 and to Tetrahydrofuryl-1-butanol-3.—A solution of 55 g. of pure fural-acetone in 150 cc. of 95% alcohol was reduced in the presence of 1 g. of catalyst. The first molecular equivalent of hydrogen was ab-

sorbed in 20 minutes. The catalyst was reactivated and the second molecular equivalent of hydrogen was absorbed in 30 minutes. Again the catalyst was reactivated and the third molecular equivalent of hydrogen was absorbed in 70 minutes. The reduction in a number of experiments was stopped at this point. In other experiments the catalyst was again reactivated and the absorption carried on until a fourth molecular equivalent of hydrogen had been taken up. The absorption of this last molecular equivalent generally required between 8 and 15 hours with several reactivations of the catalyst. When the reduction was stopped after the absorption of 3 molecular equivalents, practically a quantitative yield of the ketone was obtained, and when four molecular equivalents were absorbed practically a quantitative yield of the alcohol was obtained.

Tetrahydrofuryl-1-butanone-3,  $C_4H_7O$ — $CH_2CH_2COCH_3$ —In the reduction of 55 g. of fural-acetone it was not difficult to obtain 40 g. of completely purified tetrahydrofuryl-1-butanone-3. The ketone was a water-clear liquid of pleasant odor, which gradually became yellowish on standing. It was insoluble in water but readily soluble in alcohol and ether. It boiled at 81° (2 mm.);  $n_p^{19}$ , 1.4459;  $d_{20}^{20}$ , 0.9815.

Analyses. Subs., 0.2055:  $CO_2$ , 0.5065;  $H_2O$ , 0.1763. Calc. for  $C_8H_{14}O_2$ : C, 67.55; H, 9.93. Found: C, 67.22; H, 9.60.

Tetrahydrofuryl-1-butanol-3,  $C_4H_7O$ — $CH_2CH_2CHOHCH_3$ .—From 55 g. of fural-acetone 42 g. of absolutely pure alcohol could readily be obtained. It was a colorless, odorless liquid which did not become colored on exposure to air. It was practically insoluble in water but soluble in alcohol and ether. It boiled at 93–94° (2 mm.);  $n_D^{19}$ , 1.4546;  $d_{20}^{20}$ , 0.9774.

Analyses. Subs., 0.2182:  $CO_2$ , 0.5343;  $H_2O$ , 0.2244. Calc. for  $C_6H_8O_2$ : C, 66.61; H, 11.19. Found: C, 66.78; H, 11.51.

Fural-acetophenone to Tetrahydrofuryl-1-phenyl-3-propanone-3 and Tetrahydrofuryl-1-phenyl-3-propanol-3.—The reduction took place rapidly as in the case of the fural-acetone. It was possible to reduce 25 g. of pure fural-acetophenone in 75 cc. of alcohol with 0.5 g. of catalyst until three molecular equivalents of hydrogen had been absorbed in about 2 hours, with only one reactivation of the catalyst. The absorption of the fourth molecular equivalent of hydrogen required about 8 hours and two reactivations of the catalyst. The yields of ketone after three molecular equivalents of hydrogen had been absorbed, and of alcohol after four equivalents had been absorbed, were practically quantitative.

Tetrahydrofuryl-1-phenyl-3-propanone-3,  $C_4H_7O$ — $CH_2CH_2COC_6H_5$ .—From 25 g. of fural-acetophenone 18 g. of perfectly purified ketone was obtained boiling at 153–154° (2 mm.);  $n_D^{20}$ , 1.4885;  $d_{20}^{20}$  1.0913. It was a practically colorless liquid, insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.3050: CO₂, 0.8577; H₂O, 0.2056. Calc. for C₁₃H₁₆O₂; C, 76.42; H, 7.90. Found: C, 76.69; H, 7.54.

Tetrahydrofuryl-1-phenyl-3-propanol-3,  $C_4H_7O$ — $CH_2CH_2CHOHC_6H_6$ .—From 25 g. of fural-acetophenone about 21 g. of absolutely purified alcohol was obtained boiling at 167–168° at 2 mm.;  $n_2^{20}$ , 1.5245;  $d_{20}^{20}$ , 1.0601. It was a water-clear liquid, insoluble in water but soluble in alcohol and ether.

Analyses. Subs., 0.2697:  $CO_2$ , 0.7490;  $H_2O$ , 0.2145. Calc. for  $C_{12}H_{18}O_2$ : C, 75.67; H, 8.80. Found: C, 75.74; H, 8.90.

#### Summary

1. The reduction of furfural in alcohol solution, using platinum oxide as a catalyst, has been studied. By the absorption of one molecular equivalent

of hydrogen, furyl alcohol is obtained in quantitative yields. When the reduction is carried further, 2.3 to 3.3 additional molecular equivalents of hydrogen are absorbed with the formation of a mixture of four products; tetrahydrofuryl alcohol, pentanediol-1,2, pentanediol-1,5 and *n*-amyl alcohol. The first of these is formed in largest amounts and the amounts of the others decrease in the order given.

- 2. It has been found that platinum oxide from spectroscopically pure chloroplatinic acid or c. p. chloroplatinic acid of commerce is a very ineffective catalyst toward the reduction. In the presence of small amounts of ferrous chloride, however, the reduction takes place very rapidly. A series of experiments using increasing amounts of ferrous chloride showed an increase in the speed of reduction up to a certain maximum beyond which larger amounts caused a diminution in speed. The larger amounts of ferrous chloride have a greater poisoning effect on the platinum as a catalyst toward the reduction of the ethylene linkages in the furane ring than toward the reduction of the aldehyde group.
- 3. The amount of ferrous chloride which afforded a maximum activity for a certain weight of platinum catalyst produced the same activity when double the amount of platinum and double the amount of reagents were used.
- 4. Platinum catalyst that has been redissolved and reprecipitated as oxide a number of times accumulates a certain amount of impurity so that it is active for the reduction of furfural without the addition of ferrous chloride. The activity of such catalyst, however, is much less than the activity in the presence of a little ferrous chloride.
- 5. The distinct advantage of using oxygen in place of air for reactivation of the catalyst has been demonstrated.
- 6. The best method for reducing furfural found in this research was by the use of 50 g. of furfural, 150 cc. of alcohol, 1 g. of catalyst and 1.2 cc. of 0.1 M ferrous chloride. Using hydrogen under 1 to 2 atmospheres' pressure the absorption of about 4 molecular equivalents of hydrogen took place in 4 hours. Three reactivations of the catalyst were made with oxygen during this period. This is in contrast to the reduction of furfural described by a previous investigator where 48 g. of furfural was used and 285 hours and 10 additions of fresh catalyst were required for the reduction.
- 7. By the use of the platinum oxide catalyst, furfural derivatives were readily reduced; pyromucic acid was converted to tetrahydro-pyromucic acid; ethyl pyromucate to ethyl tetrahydro-pyromucate;  $\beta$ -furyl-acrylic acid to  $\beta$ -tetrahydrofuryl-propionic acid; furoin to two stereo-isomeric dihydroxy-1,2-di-(tetrahydrofuryl)-1,2-ethanes; fural-acetone to tetrahydrofuryl-1-butanone-3 and to tetrahydrofuryl-1-butanol-3; fural-acetophenone to tetrahydrofuryl-1-phenyl-3-propanone-3 and tetrahydrofuryl-1-phenyl-3-propanol-3.

URBANA, ILLINOIS

[Contribution from the Chemical Laboratories of Columbia University, No. 418]

# THE ACTION OF SULFUR UPON PARA-TOLUIDINE IN THE PRESENCE OF LITHARGE. THIO-PARA-TOLUIDINE, ITS CONSTITUTION AND SOME NEW DERIVATIVES

By Marston Taylor Bogert and Malvin R. Mandelbaum Received August 21, 1923

#### Introductory

When p-toluidine and sulfur are heated together, various products are formed depending upon the proportions of initial materials, temperature and duration of the heating, presence or absence of such hydrogen sulfide absorbents as litharge, and other factors. The commercially important products are dehydrothio-p-toluidine and primuline, but one of the simplest is the "thio-p-toluidine" first isolated by Merz and Weith from a melt obtained by heating p-toluidine with sulfur at  $140^{\circ}$  in the presence of litharge.

The literature concerning the structure of this latter compound is inconclusive and contradictory. Merz and Weith merely gave the molecular formula as C₁₄H₁₆N₂S. In fact, they even failed to state until 15 years later^{2,3} which toluidine they used. Truhlar⁴ investigated the compound quite extensively, at the request of Professor Merz, and prepared a large number of derivatives, but did not commit himself further regarding the constitution of the base than to write the formula as (CH₃.C₆H₃.NH₂)₂S and to propose the name "amidothio-p-tolyl." Dahl and Co.3,5 patented certain of the azo dyes obtainable from this amine, characterizing the base as "thio-p-toluidine (of melting point 103°)." Green, however, adopted Formula II, but without citing any experimental proof in support thereof, and expressed the opinion that it was the antecedent substance from which both dehydrothio-p-toluidine and primuline were formed by further action of sulfur, since he had actually obtained7,8 primuline from it in this way. Subsequently he changed his views regarding the origin of the dehydrothio-p-toluidine and suggested a different explanation. In 1890, Purgotti¹⁰ removed the amino groups through the diazo reaction and stated that he obtained a di-o-tolyl sulfide, from which he concluded that the Merz

- ¹ Merz and Weith, Ber., 4, 393 (1871).
- ² Merz and Weith, Ber., 19, 1571, footnote (1886).
- ³ Dahl and Co., Ger. pat. 34,299; Friedlaender, 1, 534 (1885).
- ⁴ Truhlar, Ber., 20, 664 (1887).
- ⁵ Dahl and Co., Brit. pat., 14,232 (1885).
- 6 Green, J. Chem. Soc., 55, 233 (1889).
- 7 Ref. 6, p. 227.
- ⁸ Green, Ber., 22, 968 (1889).
- ⁹ Green, Thorpe's, "Dictionary of Applied Chemistry, Longmans and Co., 1913, vol. 4, p. 386.
  - 10 Purgotti, Gazz. chim. ital., 20, 31 (1890).

and Weith base should be represented by Formula III. Beilstein¹¹ gives the preference to Formula II.

Hence, it seemed to us worth while to study this problem somewhat more fully, so as to establish definitely the constitution of the Merz and Weith base and to determine under what conditions, if any, it could be converted into dehydrothio-p-toluidine. As set forth in what follows, we believe that we have solved the first of these two problems, but the work upon the second is unfinished and the report thereon must be deferred to a later communication.

The plan of attack involved the preparation of the base by the Merz and Weith method, examination of the product and comparison of the same with ditolyl sulfides synthesized in other ways.

In the repetition of the process of Merz and Weith, it was found far more satisfactory to isolate the products from the crude melt by a method which rested upon the assumption of a sufficient difference in basicity to permit their successive extraction from a benzene solution by a series of acids each stronger than its predecessor. In this way, p-toluidine, thio-p-toluidine and dithio-p-toluidine were isolated.

Purgotti¹⁰ prepared di-o-tolyl sulfide (o-cresyl sulfide) from o-toluidine by the customary diazo-reaction, and described his product as an oil, boiling at 285°. Since the product he obtained by de-amination of the Merz and Weith base was similar in appearance and boiled at 284–286°, the two were regarded as identical, although he gave no analytical data or other criteria of purity or of identity. Both Zeiser¹² and Mauthner, ¹³ however, have since shown that pure di-o-tolyl sulfide is a solid, which melts at 64° and boils at 174° at 15 mm. pressure. Purgotti's product, therefore, must have been either very impure or something else. Mauthner prepared also the di-m-tolyl sulfide as a colorless oil, boiling at 174° at 12 mm. pressure, and the o-tolyl-m-tolyl sulfide as a colorless and odorless oil, boiling at 170° at 11 mm. pressure. There is thus but little difference in the boiling points of the three isomers and, as a means of identifying such isomers, it is consequently of little value.

On repeating Purgotti's experiment for the elimination of the amino groups from the Merz and Weith base, much difficulty was encountered in our efforts to get a product of unquestionable purity. Our lack of success here corresponded with that of Truhlar, who found it impossible to replace the amino groups by halogen or cyanogen through the diazo reaction, although he did succeed in getting the phenol finally.

The sulfide obtained from the Merz and Weith base by de-amination

¹¹ Beilstein, "Handbuch der Organischen Chemie," Leopold Voss, 3d ed., 1903, II, 821, and Suppl., II, 483.

¹² Zeiser, Ber., 28, 1674 (1895).

¹³ Mauthner, Ber., 39, 3595 (1906).

therefore was easily oxidized to the sulfone, forming colorless crystals melting sharply at 94°, and whose analysis gave figures agreeing closely with those calculated for a ditolyl sulfone. Di-o-tolyl sulfone has been reported¹⁰ as melting at 134–135°, and the di-p-tolyl isomer¹⁴₁⁵ at 158°, but we failed to find in the literature any record of the di-m-tolyl sulfone. It is obvious, however, that Purgotti was in error in concluding that the sulfide obtained by de-aminating the Merz and Weith base was the di-o-tolyl compound, as he would have discovered very quickly himself had he carried his work one step farther and oxidized it to the sulfone.

It remained, then, to check the accuracy of the deduction that our sulfone melting at 94°, and its antecedent sulfide, were actually the *meta* compounds, and this was accomplished by synthesizing di-m-tolyl sulfide from m-iodotoluene and sodium m-thiocresylate. In this undertaking, it was found advantageous to prepare the necessary m-thiocresol from benzaldehyde-m-sulfo acid, rather than by the methods hitherto recorded in the literature. When this synthetic di-m-tolyl sulfide was oxidized, it yielded a sulfone identical in appearance with that obtained from the deaminated Merz and Weith base and which also melted sharply at 94°. An intimate mixture of the two melted at the same point.

Further, among the by-products of the thio-p-toluidine melt, there was found a yellowish-brown, waxy solid, which formed a beautifully crystalline acetyl derivative, melting at 213° (corr.). The analysis of this acetyl derivative showed that it contained carbon and hydrogen in the proportion present in a bis(acetaminotolyl) disulfide, (CH₃CONH(CH₃)C₆H₃)₂S₂. Jacobson and Ney¹⁶ have described the diacetyl derivative of bis(2-amino-5-methylphenyl) disulfide (V) as crystallizing in similar form and as melting at 204–206°.

These facts seem to us to justify the conclusion that thio-p-toluidine should be represented by Formula II, and not by III. Of course, this does not exclude the possibility of III, or even IV, being formed also in the thio-p-toluidine melt, but we have uncovered no proof of their presence or of dehydrothio-p-toluidine. Nor have we encountered either p-amino dithiobenzoic acid,  $H_2NC_6H_4CSSH$ , or its p-toluidide, which Green suggested as intermediate products in the conversion of p-toluidine into dehydrothio-p-toluidine. It is quite likely, on the other hand, that small amounts of stilbene derivatives are formed in this reaction, since Aronstein and van Nierop¹⁷ found that on long (120 hours) boiling of toluene with sulfur, hydrogen sulfide was liberated and some stilbene produced,

¹⁴ Otto and Beckurts, Ber., 11, 2068 (1878).

¹⁵ Crafts, Ber., 12, 1177 (1879).

¹⁶ Jacobson and Ney, *Ber.*, **22**, 908 (1889). See also Rassow and Reim, *J. prakt. Chem.*, [2] **93**, 216 (1916).

¹⁷ Aronstein and van Nierop, Rec. trav. chim., 21, 450 (1902).

and our own experiments have demonstrated the fact that sulfur acts much more vigorously upon toluene in the presence of litharge, or other hydrogen sulfide absorbents, likewise with formation of stilbene.

Our experiments then indicate that when p-toluidine is heated with sulfur, in the presence of litharge and at a temperature of 140-145°, the main course of the reaction is the formation first of the mercaptan (I). This, then, through the simultaneous oxidizing influence of sulfur and litharge. unites with unchanged p-toluidine to thio-p-toluidine (II), while small amounts (generally not over 5%) escape this reaction and are oxidized directly to the disulfide (V). In the absence of litharge, and at the higher temperatures employed (180-220°) for the manufacture of dehydrothiop-toluidine and primuline, the mercaptan condenses with the methyl group of unchanged p-toluidine, instead of with its nuclear hydrogen, thus generating a compound which is more stable than thio-p-toluidine under these conditions of temperature. This deduction as to the course of the reaction by which dehydrothio-p-toluidine (VI) is formed from p-toluidine and sulfur, is in accord with the surmise of Friedlaender. 18 Conversely, Gattermann and Pfitzinger¹⁹ have shown that when dehydrothio-ptoluidine is fused with potassium hydroxide, it is hydrolyzed to the mercaptan (I) and p-aminobenzoic acid. Schultz and Beyschlag20 treated m-tolylene diamine with sulfur in boiling alcohol solution and obtained a bis(2,4-diamino-5-methylphenyl) polysulfide, proving that here also the sulfur entered meta to the methyl group and ortho to the amino.

We have tried in vain to convert thio-p-toluidine into dehydrothio-p-toluidine by the action of heat alone, and also in the presence of sulfur or of p-toluidine. These experiments are being continued since, as already mentioned, Green obtained primuline from thio-p-toluidine and sulfur. The explanation of this apparent discrepancy may lie in the fact that "primuline" is really the name not of a chemical individual but of a group of compounds of high molecular weight, produced from p-toluidine and sulfur at elevated temperatures, through elimination of varying amounts of hydrogen sulfide. The manner in which the p-toluidine residues combine, and the number of residues so uniting, differ considerably, but all have certain tinctorial properties in common. The constitution of most of them is still unknown.

Through its diacetyl derivative, thio-p-toluidine was oxidized to bis(2-acetamino-5-carboxyphenyl) sulfone, which was then de-acetylated (VII) and the product esterified. It is hoped that some of the esters so accessible may exhibit the local anesthetic properties characteristic of p-aminobenzoic esters (benzocaine, propaesin, cycloform, etc.), for the physio-

¹⁸ Friedlaender, Fortschritte Teerfarb., 7, 481 (1905).

¹⁹ Gattermann and Pfitzinger, Ber., 22, 1066 (1889).

²⁰ Schultz and Beyschlag, Ber., 42, 743 (1909).

logical effects of the sulfonals appear to depend mainly upon the alkyl groups present and not upon the sulfone bridges.

The disulfide (V) corresponding to thio-p-toluidine was discovered by Jacobson and Ney. It is a homolog of the bis(2-aminophenyl) disulfide originally described by Hofmann and recently put upon the market as a remedy for syphilis under the name of "Intramin." The isomeric disulfides from 2-amino-4-methylphenyl mercaptan and 4-amino-2-methylphenyl mercaptan are also known. It is a matter of some historical interest that the diacetyl derivative of dithio-p-toluidine (V) agrees closely in crystalline form, solubilities and melting point, with what Truhlar thought was the diacetyl derivative of thio-p-toluidine itself. Our experiments have shown that when crude thio-p-toluidine, containing even very small amounts of the disulfide, is acetylated, it is the diacetyl derivative of the disulfide which separates immediately and not that of thio-p-toluidine. This would account for Truhlar's error, except for the fact that his analytical figures check for the mono- and not for the disulfide derivative.

**Experimental Part** 

Fusion of p-Toluidine and Sulfur, and Treatment of the Crude Melt.—The claim of the Dahl patent³ that a yield of thio-p-toluidine amounting to about 60% of that

²¹ Hofmann, Ber., 12, 2363 (1879).

²² Ber., 42, 4310 (1909).

²³ Ber., 45, 1496, 1501 (1912).

calculated can be obtained by the Merz and Weith process is not in agreement with our experience, for our yields of pure product (m. p., 103-104° corr.) were invariably far below that figure. We found it advisable, therefore, to modify the method somewhat, as explained in what follows.

A mixture of  $1070 \, \mathrm{g}$ . of p-toluidine (10 moles) and 320 g. of sulfur (10 equivalents) was melted in a suitable flask, and the temperature of the melt raised gradually to  $140-145^{\circ}$ , where it was maintained while litharge was added slowly in small amounts and with vigorous stirring, until further addition no longer caused effervescence or rise of temperature. Usually, this condition was attained after some  $1600 \, \mathrm{g}$ . of litharge had been added during  $6 \, \mathrm{hours}$ .

In most cases, the reaction proceeded quite smoothly with evolution of steam, but occasionally the flask boiled over without apparent cause. This was due neither to the rate of addition of the litharge, nor to any detectable impurity in the latter.

The presence of iron or nickel wool (sometimes partially oxidized), or substitution of other oxides or carbonates for the litharge, with the object of providing an absorbent for hydrogen sulfide which would not react as rapidly with free sulfur, failed to improve the yield of final product. With ferric or zinc oxide, no reaction occurred even at 165°. With lead carbonate, a reaction took place at 165–170°, but the higher temperature necessary offset any advantage which might have been inherent in this substitution.

It seemed not unlikely that the thio-p-toluidine as formed was attacked by the unchanged sulfur present and that the velocity of this decomposition was determined by the concentrations of thio-p-toluidine and of sulfur, and the temperature and duration of the heating. Under the conditions noted above, equilibrium appeared to have been reached when the amount of thio-p-toluidine present was such as to give a final yield of approximately 30% of that calculated from the p-toluidine actually consumed in the operation. In support of this assumption, it was found that an increase in the amount of sulfur used in the reaction resulted in no increase in the yield of thio-p-toluidine, but a decrease in the weight of p-toluidine recovered and the formation of more tarry by-products. Similarly, any considerable prolongation of the heating after the requisite amount of litharge had been added tended to diminish the yield.

Upon completion of the reaction, the melt was agitated with 3 to 4 liters of boiling 95% alcohol, some "Sil-o-Cel" added, and the mixture filtered hot, giving a dark brown filtrate. Addition of an alcoholic solution of oxalic acid to this filtrate precipitated the p-toluidine quantitatively as oxalate, free from sulfur compounds, and proved a rapid and convenient way of following the progress of the reaction in the smaller scale preliminary experiments. It was not the best way, however, of recovering the p-toluidine in the major runs, when it was desired to isolate also the other products of the reaction. The usual method of procedure was to distil the alcohol from this filtrate, take up the residue in benzene and extract the benzene solution with acids of increasing strength. Benzene was not used for the preliminary extraction of the melt, since it rendered the filtration from the lead sulfide sludge much more tedious and troublesome. The residue obtained by evaporating the alcohol from the filtrate mentioned, amounting to about 1080 g. generally (equivalent to 88% of the combined weight of initial p-toluidine plus half the sulfur), was poured into 1500 cc. of benzene.

Extraction of the benzene solution with aqueous solutions of different acids was carried out in a tall cylinder equipped with a mechanical stirrer and siphon, for this was found to be more satisfactory than the use of a large separatory funnel.

An unstable salt with one of the products of its hydrolysis constantly withdrawn into another phase should be almost completely hydrolyzed, while a more stable one, under identical conditions would remain but little affected. Hence, in the case of two immiscible solvents, such as benzene and water, in one of which the free base is the more soluble, and in the other the salt, it should be possible to extract a benzene solution of

free bases with aqueous solutions of suitable acids, thus forming a series of salts of which only those of the stronger bases would be stable in the presence of the other phase and remain in the aqueous extract. Thus, by selection of the proper acids, of gradually increasing ionization constants, the attempt was made to extract the various bases seriatim. In the absence of exact quantitative data concerning the strength of the bases to be extracted, it was assumed that the order of basicity was probably p-toluidine > thio-p-toluidine > dithio-p-toluidine. The acids chosen were acetic (k = 0.000018), citric (k = 0.00081), tartaric (k = 0.00109), oxalic (k = 0.10), and sulfuric. These values for k are all at the uniform temperature of 25°. Dilute (15%) acetic acid failed to extract all of the p-toluidine. Dilute (15%) citric acid extracted practically all of the p-toluidine, with only traces of thio-p-toluidine. Tartaric acid likewise extracted the p-toluidine, but formed with it a more difficultly soluble salt and so was less satisfactory.

Successive extractions of the benzene solution were conducted, therefore, with 1 liter portions of dilute (15-20%) citric acid, and the temperature was kept at  $25^{\circ}$  to avoid separation of p-toluidine citrate, which is rather difficultly soluble at lower temperatures. The separated extracts were neutralized with ammonia, and p-toluidine was precipitated in small colorless crystals. Those obtained from the first extraction often showed a reddish tinge, due to traces of an impurity which possessed the properties of an indicator, giving a yellow solution with acids and a red one with bases. When further extraction with citric acid yielded on neutralization only a slight turbidity, the remaining citric acid was removed from the benzene layer by washing it once with water. Five or six extractions in this way with citric acid yielded 320 g. of pure p-toluidine.

The benzene layer was extracted next with a saturated aqueous solution of oxalic acid, also used in 1-liter portions. The yellow extracts were united and diluted with at least an equal volume of water, to provide for the rather low solubility of ammonium oxalate, and then neutralized with ammonia. The crude thio-p-toluidine thus precipitated was light yellow and fairly pure (m. p., about  $100^{\circ}$ ), except that separated from the final extraction, which was apt to be colored a darker yellow from contamination by small amounts of the disulfide. Four or five extractions yielded 276 g. of crude thio-p-toluidine, equivalent to 32% of that calculated after allowing for the p-toluidine recovered. Since p-toluidine oxalate is but slightly soluble in water or the more common organic solvents, it was very easy to determine whether any p-toluidine had escaped the citric acid extraction.

During the final oxalic acid extractions, a heavy viscous tar separated in the extraction cylinder, thus giving a 3-phase system, composed of an upper benzene layer, an intermediate aqueous oxalic acid layer, and a lower one of tar. After siphoning off the oxalic layer, the benzene layer and tar were washed with water, the water was separated and the benzene layer decanted from the tar.

Extraction of the benzene layer was then resumed, using dilute (10%) sulfuric acid. Neutralization of the sulfuric acid extracts gave 40 g. of a yellow, waxy solid, which proved to be the crude disulfide (V). The yield of this never exceeded 5% of the weight of the p-toluidine entering into reaction. Some tar separated also in these extractions.

The extracted benzene solution was finally evaporated and the dark viscous residue boiled with concd. hydrochloric acid and filtered. When this hydrochloric acid extract was poured into water, a small amount of yellow solid precipitated, but it was not dehydrothio-p-toluidine (VI), for its alcoholic solution exhibited no fluorescence.

The tar separated during the oxalic acid extractions was digested with fresh benzene, in the presence of a 5% sodium hydroxide solution, to recover any organic bases present. The benzene layer was separated and the solvent driven off. There remained 35 g. of a heavy, greenish oil. The tar separating from the sulfuric acid extractions was treated similarly, and yielded 70 g. of a dark bluish oil. Neither acetyl nor benzoyl derivatives could be prepared from either of these oils. Addition of phenyl isocyanate to their

benzene solutions precipitated amorphous solids, insoluble in the usual organic solvents, with the exception of nitrobenzene, from which they deposited in a greenish, pulverulent form.

Thio-p-toluidine (II).—The crude thio-p-toluidine, obtained as described above, was dissolved in hot dil. (10%) hydrochloric acid, and to this hot solution coned. hydrochloric acid was added until precipitation began. As the solution cooled, pale yellowish needles of the hydrochloride separated. These were dissolved in hot water, the solution was heated with animal charcoal, filtered, and ammonia added in excess to the filtrate. Thio-p-toluidine separated as a pale yellow powder, melting at 102–103°, sufficiently pure for most purposes. The yield was 80% of the crude substance. A single crystallization from dil. alcohol gave a pure product in lustrous, colorless scales; m. p., 103–104° (corr.). This melting point was not altered by further crystallization and agrees with that reported by other investigators.

The picrate, benzoyl derivative (m. p., 186°), and urethan (m. p., 113°), were also prepared and agreed entirely with Truhlar's description of them.

Diacetyl Derivative.—This was obtained by the action of acetic anhydride, or of acetyl chloride, upon the base. It crystallized from alcohol in large rhombic plates; m. p., 165° (corr.).

Analyses. Calc. for  $C_{18}H_{20}O_2N_2S$ : C, 65.85; H, 6.10; S, 9.76. Found: C, 65.76, 65.85; H, 5.91, 5.78; S, 9.46.

As noted in the introductory portion of this paper, this product is not the same as the one (m. p., 211°) which Truhlar believed to be the diacetyl derivative of thio-p-toluidine, nor have we been able to obtain his product from pure thio-p-toluidine, although many different methods of acetylation were applied.

Di-m-tolyl Sulfide.—Forty-one g. of thio-p-toluidin was dissolved in 200 cc. of alcohol, 28 cc. of coned. sulfuric acid added, and the mixture warmed until a clear solution resulted. This solution was stirred vigorously during preliminary cooling, so that whatever sulfate separated would be in a finely divided state. The mixture was then further cooled to 0-5°, and maintained at that temperature, with constant stirring, while a solution of 27.2 g. of sodium nitrite in 45 cc. of water was run in slowly. After all the nitrite had been added, the dark red solution was left at 0° for 3 hours. Four g. of copper powder was then added. A slow evolution of gas commenced immediately and the temperature of the solution gradually rose. After standing overnight at laboratory temperature, the solution was boiled for 2 hours under a reflux condenser and then distilled at 100°, to remove aldehyde, alcohol and water. The tarry residue was extracted with chloroform, the extracts dried over calcium chloride and fractionated under diminished pressure. Six and a half g. of a pale amber, highly refracting oil was thus secured, boiling at 197° (23 mm.), 200° (25 mm.), and 202° (28 mm.). Purgotti¹⁰ reported the boiling point of the ditolyl sulfide obtained by him from thio-p-toluidine (by the action of nitrous acid and alcohol) as 284-286° at atmospheric pressure, but gave no further information concerning his process or product, other than the bald statement that its analysis (not given) and other properties (not specified) proved it to be the di-o-tolyl sulfide (o-cresyl sulfide), identical with that prepared by him from o-toluidine.

In order to secure a di-m-tolyl sulfide of high purity, benzaldehyde-m-sulfo acid was converted into the benzalchloride-m-sulfochloride, which was reduced to m-thiocresol, and the sodium salt of the latter then condensed with m-iodotoluene in the presence of copper powder. This process starts with readily accessible materials, is neither difficult nor laborious, and gives an excellent yield of water-clear thiocresol.

Of the methods utilized by other investigators, toluene-m-sulfochloride²⁴ is not so easily obtainable, while the employment of m-toluidine as initial material is expensive

²⁴ Huebner and Post, Ann., 169, 51 (1873).

and involves some risk of explosion in the conversion of the diazonium salt to the thiocresol through the xanthogenate. ²⁵

Benzaldehyde-m-sulfo acid was made from benzaldehyde and fuming sulfuric acid, by the method of Wallach and Wuesten. Fifty-five g. of the aldehyde yielded 85 g. of the sodium m-sulfonate. From the dry salt and phosphorus pentachloride the crude benzalchloride-m-sulfochloride was obtained. This was reduced directly by zinc dust and dil. sulfuric acid at 0°, giving the m-thiocresol as a colorless, highly-refracting liquid, of extremely disagreeable odor; b. p., 195°; yield, 18 g. from 75 g. of the sodium m-sulfonate, or 40%.

One g. of metallic sodium was dissolved in 18 cc. of absolute alcohol, 5.7 g. of m-thiocresol added and the alcohol distilled. To the residual, colorless solid were added 0.2 g. of copper powder and 10.6 g. of m-iodo-toluene, and the whole was heated for several hours at 235-240°. When cold, the mixture was treated with alcohol, the alcoholic solution acidified with sulfuric acid, some zinc dust added, and steam blown through as long as it carried over any oily distillate. The residual sludge was extracted with ether, the ethereal solution dried over calcium chloride and distilled. Three g. of di-m-tolyl sulfide was thus obtained as a pale yellowish, highly-refracting oil; b. p., about 290°. This is essentially the method of Mauthner. 13

Di-m-tolyl Sulfone.—The di-m-tolyl sulfide thus synthesized was suspended in boiling 40% acetic acid and oxidized carefully by gradual addition of 5 g. of powdered potassium permanganate. The sulfone as formed collected with the manganese oxide sludge, from which it was extracted by alcohol. On crystallization from the same solvent, it was obtained in colorless needles; m. p., 94°. Five g. of the sulfide yielded 3 g. of the sulfone.

Similar treatment of the ditolyl sulfide resulting from the de-amination of thio-p-toluidine gave a sulfone of the same appearance and melting point. An intimate mixture of the two also melted sharply at 94°. This sulfone from the thio-p-toluidine was analyzed.

Analyses. Calc. for  $C_{14}H_{14}O_2S$ : C, 68.29; H, 5.69. Found: C, 68.27, 68.19; H, 5.69, 5.51.

Bis(2-aceto-amino-5-methylphenyl) Sulfone,  $(CH_3CONH(CH_3)C_6H_3)_2SO_2$ .—Fortyfour g. of thio-p-toluidine was acetylated with 45 cc. of acetic anhydride, and the reaction product poured into a solution of 300 cc. of glacial acetic acid in 400 cc. of water. The resulting solution was heated to boiling, and 48 g. of potassium permanganate dissolved in 250 cc. of hot water was added gradually in small amounts. The oxidation ensued rapidly and the solution was filtered hot from precipitated manganese oxides. Some of the sulfone crystallized from the filtrate as it cooled, and more was recovered therefrom by partially neutralizing the solution with ammonium hydroxide. From the precipitated manganese oxides also some was collected by extraction with alcohol. The total amount obtained was 35 g. It crystallized from alcohol in long prismatic needles; m. p.,  $225^{\circ}$  (corr.).

Analyses. Calc. for C₁₈H₂₀O₄N₂S: C, 60.00; H, 5.55. Found: C, 60.37; H, 5.66. Three g. of this sulfone was heated for several hours at 180° with 15 cc. of concd. sulfuric acid, and then for 30 minutes longer at 300°. The cooled solution was poured upon twice its volume of ice. A small amount of tar separated and was removed. By further dilution of the filtrate, 2 g. of yellow solid was precipitated, which proved to be the de-acetylated sulfone (m. p., 206°) described beyond. No toluidine sulfo acids were found among the products.

²⁵ Bourgeois, Rec. trav. chim., 18, 449 (1899).

²⁶ Wallach and Wuesten, Ber., 16, 150 (1883).

²⁷ Ger. pat. 239,311; Chem. Zentr., 1911, II, 1394.

Bis(2-amino-5-methylphenyl) Sulfone.—The diacetyl derivative was hydrolyzed by boiling it with dil. (15%) sulfuric acid until a clear solution resulted. This warm solution was poured with stirring into an excess of ammonium hydroxide solution. The amino sulfone separated as a yellow powder, and was crystallized from alcohol, when it appeared in yellow granular crystals, melting at 210° (corr.), practically insoluble in water or in dilute acids; yield, 6 g. from 8.5 g. of the diacetyl derivative.

Analyses. Calc. for C₁₄H₁₆O₂N₂S: C, 60.87; H, 5.80. Found: C, 61.17, 60.77; H, 6.32, 5.99.

Bis(2-aceto-amino-5-carboxyphenyl) Sulfone.—Ten and eight-tenths g. of finely pulverized diacetyl-thio-p-toluidine (m. p., 165°) was added to a solution containing 32 g. of potassium permanganate and 24 g. of magnesium sulfate in 750 cc. of water. The mixture was boiled under a reflux condenser until the color of the permanganate was discharged, when it was filtered hot and the hot filtrate acidified with sulfuric acid. Eight g. of the dicarboxylic acid separated as a fine, white precipitate, insoluble in the common neutral organic solvents. It was purified by washing it with hot alcohol and then with ether, and showed a melting point (with decomposition) above 360°.

Analyses. Calc. for C18H16O8N2S: C, 51.43; H, 3.86. Found: C, 50.56, 52.48; H, 3.83, 4.07.

Bis(2-amino-5-carboxyphenyl) Sulfone (VII).—The free amino acid was prepared from its diacetyl derivative by boiling the latter with dil. (10%) sodium hydroxide solution and precipitating the filtrate with dil. hydrochloric acid. It was difficultly soluble in the ordinary organic solvents and likewise melted above 360° with decomposition.

Methyl Ester .- As obtained from the acid, methyl alcohol and hydrogen chloride, it crystallized from alcohol in thin, square, colorless tablets with ridged diagonals; m. p., 234° (corr.).

Analyses. Calc. for C₁₆H₁₆O₆N₂S: C, 52.70; H, 4.40. Found: C, 52.85, 52.94; H, 4.49, 4.67.

Ethyl Ester.—This was obtained as yellowish, transparent prisms (from alcohol): m. p., 206° (corr.).

Analyses. Calc. for C₁₈H₂₀O₆N₂S: C, 55.10; H, 5.10. Found: C, 55.14; H, 5.09.

Structurally, these esters are composed of two benzocaine (anesthesine) molecules united by a sulfone (sulfuryl) bridge, and hence might be expected to exhibit some local anesthetic action. Unfortunately, the solubility of the methyl and ethyl esters was too low to cause any pronounced physiological effects, as indicated by preliminary tests. but the field is being explored further, in the hope of discovering more soluble derivatives of therapeutic value.

Bis(2-nitro-4-methylphenyl) Sulfide (VIII).-Forty g. of crystallized sodium sulfide, Na₂S.9H₂O, and 88 g. of 4-iodo-3-nitrotoluene were dissolved in 300 cc. of alcohol. and the dark brown solution boiled for 12 hours under a reflux condenser. The alcohol was distilled and the residue poured into water. On standing overnight, 27 g. of a dark red oil collected. This was washed repeatedly with dilute acid and with alkali. After several days, it solidified partially, yielding 4 g. of crystals. Re-crystallized from acetone, it appeared in large, dark red, short prisms, giving a yellow powder when crushed; m. p., 125-126° (corr.).

Analyses. Calc. for C₁₄H₁₂O₄N₂S: C, 55.26; H, 3.95. Found: C, 55.21, 55.36; H. 3.85, 3.40.

Bis(2-aceto-amino-5-methylphenyl) Disulfide.—Ten g. of the crude dithio-ptoluidine obtained from the sulfuric acid extraction of the p-toluidine sulfur melt as already described, was treated with 12 cc. of acetic anhydride. Rapid solution occurred, with evolution of considerable heat, and the entire mass soon congealed to a brown crystalline magma. This was washed with water, and then crystallized repeatedly from alcohol, giving bunches of small, snow-white, silky needles; m. p., 213° (corr.). At higher temperatures, it sublimed with decomposition.

Analyses. Calc. for  $C_{18}H_{20}O_2N_2S_2$ : C, 60.00; H, 5.55. Found: C, 60.12, 60.28; H, 5.54, 5.80.

This compound agrees in appearance, solubility and percentage composition, with the acetyl derivative obtained by Jacobson and Ney¹⁶ from the corresponding amine, except that they gave the melting point as 204–206°.

Bis(2-amino-5-methylphenyl) Disulfide (Dithio-p-toluidine) (V).—The diacetyl derivative was hydrolyzed by boiling it with concd. hydrochloric acid, the amine hydrochloride precipitating. It was dissolved in water, the base liberated by the addition of excess of ammonium hydroxide and purified by crystallization from dil. alcohol. Long, greenish needles were obtained; m. p., 88.5° (corr.). Jacobson and Ney gave its melting point as 89°.

Truhlar states that when he treated his thio-p-toluidine with a slight excess of acetic anhydride, crystals of the acetyl derivative soon appeared which when washed with water and crystallized from alcohol separated quickly and copiously in bundles of snow-white silky needles, melting at 211°.

Judging from the resemblance in melting point and other properties that what Truhlar believed to be the diacetyl derivative of thio-p-toluidine was actually the disulfide derivative, we prepared some crude thio-p-toluidine by the Merz and Weith process and subjected it to acetylation as described by Truhlar. The crystals which separated first were removed and recrystallized from alcohol, yielding small, snow-white, silky needles, melting at 213°, identical with the disulfide derivative just mentioned, and giving the disulfide (m. p., 88.5°) on hydrolysis. This same crude thio-p-toluidine, after being freed from all disulfide, yielded only the diacetyl derivative (m. p., 165°) of thio-p-toluidine recorded above.

## Summary

- 1. The structure of the thio-p-toluidine of Merz and Weith is proved to be bis(2-amino-5-methylphenyl) sulfide.
- 2. The course of the action of sulfur upon p-toluidine, in the presence of litharge and at 140–145°, is shown to lead first to the formation of 4-amino-3-mercapto-toluene, part of which oxidizes to the disulfide, while the major portion reacts with more p-toluidine, yielding thio-p-toluidine.
- 3. The acetyl derivative described by Truhlar as a thio-p-toluidine compound is probably the disulfide derivative.
- 4. Certain derivatives of di-m-tolyl sulfide are recorded, as well as a new synthesis of m-thiocresol.
- 5. New derivatives of thio-p-toluidine also have been prepared and studied.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VALE UNIVERSITY]
THE ACTION OF ALKALI ON SUBSTITUTED URIC ACIDS. I
1,3-DIMETHYL-9-PHENYL-URIC ACID

By Elizabeth Stuart Gatewood¹ Received August 23, 1923

All of the substituted uric acids are split by alkali to some extent, the amount of decomposition depending largely on the number and position of the substituents. With one exception, that of tetramethyluric acid, neither the nature of the decomposition products nor the mechanism of the reaction has been investigated up to this time. A thorough study of the action of alkali on substituted uric acids is now being made.

Of these, 1,3-dimethyl-9-phenyl-uric acid shows a smooth and interesting decomposition. The course of the decomposition and the structure of the products are considered to be as follows.

Dimethyl-phenyl-uric acid is very slowly decomposed by  $4\ N$  alkali at room temperature; the sodium salt separates on the addition of the base, and only a small part is attacked after standing for many days. At  $100^\circ$  with more dilute alkali the decomposition is more rapid, and with  $4\ N$  alkali it is instantaneous. The gas given off is methylamine and when the solution is acidified carbon dioxide is evolved. From the acid solution on standing a crystalline product separates which melts at  $250^\circ$ . Analysis shows that it has the formula  $C_{11}H_{11}O_3N_3$ .

There are three possible structures for this substance, depending on which of the methylamino groups and which of the carbonyls are lost.

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² Fischer, Ber., 30, 3012 (1897).

When warmed with alkali or even on standing about an hour with cold alkali, the product is completely decomposed to phenylurea, methylamine, oxalic acid and formic acid. The phenylurea separates after standing only 15 minutes but no oxalic acid can be detected at this point unless the solution is first warmed, showing that the formation of oxalic acid is due to a secondary reaction. Most probably, glyoxalic acid is first formed, and this is converted into oxalic acid and glycolic acid when warmed or allowed to stand for a long time with alkali.

On the basis of this decomposition, Structure III for  $C_{11}H_{11}O_3N_3$  must be excluded, as there is no possibility of the formation by hydrolysis of either oxalic or formic acid. Carbon dioxide and glycolic acid would be the products formed. Either of the other two structures can give these products of hydrolysis, however.

(I) 
$$CH_3NH-CO$$

$$C-NH$$

$$HOC-NC_6H_5$$
(II)  $HOOC$ 

$$C-NH$$

$$CH_3NH-C-NC_6H_6$$

$$CH_3NH-C-NC_6H_6$$

$$CH_3NH-COOH$$

$$CH_3NH-COOH$$

$$COOH$$

To decide between these structures, the substance was oxidized by hydrogen peroxide in dilute alkaline solution. A product melting at  $194-195^{\circ}$  was isolated. Its empirical formula was found to be  $C_{11}H_{11}O_4N_3$ . The most probable structural formula for this substance is IV, and such a substance can result from the alkaline decomposition product only if it has Structure I.

Furthermore, the oxidation product is itself instantly decomposed by cold alkali, and the products of decomposition are phenylurea and the methylamide of mesoxalic acid.³ On boiling with alkali the decomposition goes further. Methylamine is evolved, phenylurea separates from the alkaline solution, and mesoxalic acid can be isolated in the form of its phenylhydrazone.

One of the most interesting things about this decomposition is that the *Torrey, Ber., 31, 2162 (1898).

oxidation product is of the same type of compounds as those Biltz⁴ has obtained in his caffolide decompositions. It bears a close relationship to alloxanic acid⁵ and other similar hydantoin derivatives, for it is the methylamide of 3-phenyl-5-hydroxyhydantoin-5-carboxylic acid. This type of substance Biltz obtained from caffolide or substituted caffolides by boiling with water, and he found that they were all easily decomposed by alkali to give an amine, a urea and mesoxalic acid, just as is the oxidation product of  $C_{11}H_{11}O_3N_3$ . On reduction they gave hydantoin-carboxylic acid derivatives of Type V which differs from the structure assigned to the alkaline decomposition product,  $C_{11}H_{11}O_3N_3$ , only in having a —HC— group

instead of a—C— group.  $C_{11}H_{11}O_3N_3$  cannot, however, be such a hydantoin HOC—

derivative; it is not decomposed by alkali to a hydantoin or a hydantoin-carboxylic acid as the amides of the hydantoin-carboxylic acids have been found to be. There was the possibility that phenylhydantoin had been formed and further decomposed by alkali to phenylurea. When 3-phenylhydantoin was prepared, however, and treated with alkali, it gave only phenylhydantoic acid. The alkaline decomposition product must, therefore, be an isohydantoin derivative, namely 3-phenyl-isohydantoin-5-carboxylic acid methylamide.

The experimental part of this paper gives an account of 1,7-dimethyl-9-phenyl-uric acid which has been synthesized for the first time. Like 9-phenyl-uric acid and 7-methyl-9-phenyl-uric acid,7 it is quite stable toward alkali when boiled for a short time.

This new uric acid is 1,7-dimethyl-9-phenyl-uric acid and not 3,7-dimethyl-9-phenyl-uric acid for, as Biltz⁸ has proved, when there is only one substituting group in the pyrimidine ring, the ring closing of the pseudouric acids always takes place so that this group is in Position 1 of the uric acid. A further proof that the methyl occupies Position 1 is that methylation of 7-methyl-9-phenyl-uric acid with dimethyl sulfate gives, along with some trimethyl phenyl uric acid, the same dimethyl phenyl uric acid as obtained above, and it is well known that dimethyl sulfate always methylates first on the nitrogen whose hydrogen is least acidic.⁹

The investigation of the action of alkali on tetramethyluric acid and on

⁴ Biltz, Ber., **43**, (a) 1511, (b) 1589, (c) 1600, (d) 1618, (e) 1632 (1910); **44**, (f) 1511, (g) 1524 (1911); **46**, (h) 3407 (1913). Ann., **413**, (i) 2, (j) 56, (1917); **423**, (k) 119 (1921).

⁵ Ref. 4j, p. 68.

⁶ Ref. 4h, p. 3409. Ref. 4d, p. 1619.

⁷ Moore and Gatewood, This Journal, 45, 140 (1923).

⁸ Biltz, Ann., 413, 127 (1917); 423, 256 (1921).

⁹ Biltz, Ber., **54**, 169 (1921).

1,3,7-trimethyl-9-phenyl-uric acid is already well advanced, and work on 1,3,9-trimethyl-uric acid will be begun shortly.

In conclusion, the writer wishes to express her appreciation to Professor F. J. Moore, of the Massachusetts Institute of Technology, for his valuable advice during the course of this investigation.

## Experimental Part

### 1,3-Dimethyl-9-phenyl-uric Acid

Action of Alkali.—1,3-Dimethyl-9-phenyl-uric acid¹⁰ was prepared from the corresponding pseudo-uric acid, which was obtained by the action of phenyl isocyanate on 1,3-dimethyl-uramil.

One hundred cc. of  $4\ N$  sodium hydroxide solution was added to  $2\ g$ . of finely powdered dimethyl-phenyl-uric acid. The solution was heated gradually to boiling and boiled about half a minute, cooled slightly, and then acidified with dil. hydrochloric acid. After the solution had stood for several hours (sometimes longer), a crystalline substance started to separate. It was left overnight, and when filtered and dried gave from  $1.2\ to$   $1.4\ g$ . of phenylisohydantoin-carboxylic acid methylamide, in a yield of about 80%. It crystallized from hot water in bunches of needles which melted at  $249-250\ c$  to a clear, viscous, yellow liquid. It was recrystallized again and dried in a vacuum over sulfuric acid for analysis.

Analyses. Subs., 0.1541, 0.1511: CO₂, 0.3174, 0.3100; H₂O, 0.0677, 0.0653. Subs., 0.1411, 0.0965: N, 22.9 cc.  $(23.5^{\circ}, 759.1 \text{ mm.})$ , 15.8 cc.  $(23^{\circ}, 759.1 \text{ mm.})$ . Calc. for  $C_{11}H_{11}O_3N_3$ : C, 56.62; H, 4.76; N, 18.03. Found: C, 56.22, 56.28; H, 4.92, 4.76; N, 18.14, 18.34.

OPTICAL PROPERTIES.—Habit, rectangular plates; extinction, parallel,  $\alpha$  parallel to clongation; interference figure, biaxial, large optic angle; indices,  $\alpha = 1.571$ ,  $\gamma = 1.620$ .

The other products of decomposition, methylamine and carbon dioxide, were determined—the first as methylamine chloroplatinate and the second by absorption in soda lime.

On the addition of chloroplatinic acid to the hydrochloric acid solution of the gas evolved from the alkaline-solution, orange crystals were obtained melting at 230–233°; mixed with a known sample of methylamine chloroplatinate they melted at 233°. The optical properties were also the same: habit, thin hexagonal plates; optical orientation, isotropic; index of refraction, 1.74.

One molecular equivalent of carbon dioxide was given off when the alkaline solution was acidified.

Analysis. Subs., 2.00: CO2, 0.391 g. Calc. for 1 mol.: 0.32 g.

Dimethyl-phenyl-uric acid is only very slowly attacked by cold 4 N alkali. The sodium salt of the uric acid separates and after 20 days at room temperature most of the acid is regained when the solution is acidified. From the filtrate, on standing, a small amount of phenylisohydantoin-carboxylic acid methylamide, melting at  $240^{\circ}$ , was obtained.

The sodium salt of dimethyl-phenyl-uric acid was dried at 100-110° and analyzed. Analysis. Subs., 0.2092: NaSO₄, 0.0500. Calc. for C₁₃H₁₁O₃N₄Na: Na, 7.823. Found: 7.905.

Phenylisohydantoin-carboxylic acid methylamide when refluxed for  $1^{1}/2$  hours with acetic anhydride gave, after evaporation of the mixture to dryness and addition of

¹⁰ Ref. 7, p. 143.

ether, a product melting at 185–187°. There was not sufficient material for analysis.

The alkaline decomposition product did not react with phenylisocyanate either when heated to 165°, or in alkaline solution at 0°, showing it to be an acid amide.

Action of Alkali on Phenylisohydantoin-carboxylic Acid Methylamide.—I. One g. of the alkaline decomposition product was heated with 4 cc. of 4 N alkali and the gas given off absorbed in a little dil. hydrochloric acid. This solution gave, on the addition of chloroplatinic acid and subsequent evaporation, the characteristic orange crystals of methylamine chloroplatinate, melting at 228–230°.

Phenylurea separated from the alkaline mother solution as it cooled. It melted at 144°; mixed with a pure sample of phenylurea, it melted at 146°. The optical properties were the same: habit, plates; extinction, parallel,  $\gamma$  parallel to elongation; interference figure, biaxial, large optic angle; birefringence, weak; indices,  $\alpha=1.602$ ,  $\gamma=1.627$ . To identify the substance further as phenylurea, it was boiled with aniline, and diphenylurea was obtained in good yield. It melted at 236–238°; a mixture with a pure sample of diphenylurea, melted at 237–238°. The optical properties were identical: habit, long needles; extinction, parallel,  $\gamma$  parallel to elongation; interference figure, biaxial; birefringence, strong; indices,  $\alpha=1.620$ ,  $\gamma$ , indeterminate.

When the filtrate was acidified with acetic acid and a solution of calcium chloride added, a fine, white precipitate of calcium oxalate was obtained.

2. When  $0.1~\rm g$ . of the decomposition product was allowed to stand at room temperature with 1 cc. of 4 N sodium hydroxide, crystals of phenylurea began to separate after 15 minutes and the odor of methylamine could be detected. After half an hour the solution was filtered. The yield of phenylurea was  $0.015~\rm g$ .; m. p.,  $145^{\circ}$ . Half of the filtrate was acidified with acetic acid and a solution of calcium chloride added. The solution remained clear, showing that no oxalic acid was present. The other half was first warmed and then tested for oxalic acid as before. A precipitate of calcium oxalate separated at once.

- 3. When 0.1 g. was left at room temperature with 1 cc. of 4 N sodium hydroxide for over 1 hour, 0.02 + g. of phenylurea was obtained, and the filtrate gave calcium oxalate but the precipitate was not as heavy as in 1.
- 4. When 0.1 g. was dissolved in 8.2 cc. of water and 0.4 g. of potassium hydroxide and evaporated to dryness at  $30-40^{\circ}$ , the residue gave, after the addition of water, 0.02 g. of phenylurea (52%) and 0.035 g. of calcium oxalate (63%).
- 5. Formic acid was identified as one of the products of decomposition by its reduction of an ammoniacal solution of silver nitrate. Phenylisohydantoin-carboxylic acid methylamide was boiled with  $4\,N$  sodium hydroxide, the solution acidified with sulfuric acid and distilled. The distillate was warmed with ammoniacal silver nitrate; metallic silver was precipitated. The distillate was also tested for formaldehyde but with negative results.

Oxidation of Phenylisohydantoin-carboxylic Acid Methylamide with Hydrogen Peroxide.—On oxidation of the alkaline decomposition product with peroxide in very dilute alkaline solution, phenylurea and oxalic acid are obtained when the oxidation solution is allowed to stand for 3 hours or longer at room temperature. The decomposition is doubtless due only to the alkali, for a solution of the same concentration but without the peroxide gave the same products.

When the oxidation is allowed to proceed for only 5 minutes at 0-10° and the solution then acidified and evaporated, an oxidation product, melting at 195-196°, can be isolated. It is the methylamide of 3-phenyl-5-hydroxyhydantoin-5-carboxylic acid.

1. To 0.5 g. of the decomposition product in 6 cc. of water, 1.5 g. of solid potassium hydroxide and 35 cc. of 3% hydrogen peroxide were added. The solution was cooled and after 3 hours acidified and evaporated. A 69% yield of phenylurea and a 50% yield of calcium oxalate resulted.

2. One g. of the alkaline decomposition product was added to 12 cc. of water and cooled to 5°; 2.9 g. of potassium hydroxide and 70 cc. of 3% hydrogen peroxide were then added, and the temperature kept below 10°. After 5 minutes the solution was acidified with dil. hydrochloric acid and evaporated in a vacuum. Large clumps of material usually separated, which weighed about 0.6 g. It was purified by recrystallization from hot water many times. A little boneblack was added the first time. The pure product consisted of glistening flakes; m. p., 194–195°. It was very soluble in hot water, alcohol, acetone, and ethyl acetate, and was insoluble in ether and chloroform. It was dried in a vacuum over sulfuric acid for analysis.

Analyses. Subs., 0.1397, 0.1440:  $CO_2$ , 0.2730, 0.2795;  $H_2O$ , 0.0572, 0.0531. Subs., 0.1994, 0.1478: N, 29.6 cc. (23°, 756.7 mm.), 21.9 cc. (25°, 760.0 mm.). Calc. for  $C_1H_{11}O_4N_3$ : C, 53.01; H, 4.45; N, 16.87. Found: C, 53.28, 52.93; H, 4.58, 4.13; N, 16.56, 16.44.

OPTICAL PROPERTIES.—Habit, large, thin, rect. plates; extinction, parallel,  $\alpha$  parallel to elongation; interference figure, biaxial, large optic angle; indices,  $\alpha = 1.545$ ,  $\gamma = 1.583$ .

On further evaporation the solution gave more of the oxidation product, mixed with another substance from which it could not be completely separated. A small amount of the latter was separated mechanically. It crystallized from water in fine needles, melting at 188–190°. It was soluble in alcohol, acetone and ethyl acetate, and insoluble in ether and chloroform. It was not decomposed by alkali.

OPTICAL PROPERTIES.—Habit, needles; extinction, parallel,  $\alpha$  parallel to elongation; birefringence, strong; indices,  $\alpha=1.556$ ,  $\gamma=1.695$ .

Action of Alkali on the Oxidation Product.—1. Seven cc. of 2 N sodium hydroxide was added to 0.2 g. of the oxidation product. It dissolved at once and in a few minutes crystals began to separate. Air was passed through the solution while it was carefully heated. The gas evolved was absorbed in dil. hydrochloric acid, chloroplatinic acid added, and the solution evaporated. Orange crystals separated which melted at 228–230°; when these were mixed with methylamine chloroplatinate the melting point was not lowered. Their optical properties were the same. Phenylurea was obtained from the alkaline solution on cooling. Its melting point, 145–146°, and optical properties agreed with those of a known sample. The filtrate gave no test for oxalic acid.

2. One cc. of 4 N sodium hydroxide was added to the oxidation product. The solution was warmed carefully until the crystalline precipitate that had formed dissolved. It was then cooled, 1 cc. of water added, and the phenylurea filtered off. The yield was 0.09 g. or 90%. The filtrate was carefully neutralized with dil. acetic acid and a solution of 0.06 g. of pure phenylhydrazine in 1 cc. of water and 4 drops of glacial acetic acid added. A yellow precipitate gradually formed. The solution was warmed until clear and when cool was acidified with dil. hydrochloric acid. A heavy, yellow precipitate separated which crystallized from dil. alcohol in small, hexagonal crystals; m. p., 167°. It was very similar to the phenylhydrazone of mesoxalic acid and was at first thought to be this substance. However, on preparing mesoxalic acid by the convenient method of Chattaway and Harris, 11 and from it the phenylhydrazone, it was found that they were not the same. Mesoxalic acid phenylhydrazone was more soluble in water and crystallized in fine needles melting at 165°; when mixed with the above product the mixture melted at 150°. The optical properties also were different.

OPTICAL PROPERTIES OF THE PHENYLHYDRAZONE OF MESOXALIC ACID.—Habit, fine needles; extinction, parallel,  $\alpha$  parallel to elongation; indices,  $\alpha = 1.450$ ,  $\gamma > 1.800$ .

OPTICAL PROPERTIES OF THE PHENYLHYDRAZONE MELTING AT  $167^{\circ}$ .—Habit, hexagonal plates; extinction, symmetrical,  $\alpha$  parallel to elongation; interference figure, biaxial, large optic angle; birefringence, strong; indices,  $\alpha = 1.600$ ,  $\gamma = 1.715$ .

¹¹ Chattaway and Harris, J. Chem. Soc., 121, 2704 (1922).

It was found to be the phenylhydrazone of the methylamide of mesoxalic acid, the same substance Torrey³ obtained by the mild action of barium hydroxide on allocaffuric acid. He gives the melting point as 158°. The difference may be accounted for, however, by the well-known variation of the melting points of phenylhydrazones with rate of heating. Its solution in concd. sulfuric acid developed a red-violet color on the addition of ferric chloride; it was almost insoluble in water and, when boiled for a short time with sodium hydroxide, gave a substance melting at 205–210° (Torrey gives 205–209°). According to Biltz¹² this is the phenylhydrazone of glyoxalic acid methylamide.

3. When the oxidation product was boiled for several minutes with alkali, a strong odor of methylamine developed, and from the solution, after separation of the phenylurea and neutralization, mesoxalic acid itself was isolated as its phenylhydrazone. It crystallized from water in fine, yellow needles, melting at 160°, and mixed with a known sample gave the same melting point. The optical properties also were identical.

At one time it was thought that the oxidation product of phenylisohydantoin-carboxylic acid methylamide had the composition  $C_{10}H_{11}O_2N_3$  and that it might be the methylamide of phenyloxaluric acid,  $CH_3NHCO$ —CONHCONHC $_6H_5$ . This substance was not known, but it can be easily synthesized. Oxamethane,  13   $C_2H_5OOC$ -CONH $_2$ , when heated with phenyl isocyanate, gives the ethyl ester of phenyloxaluric acid,  $C_2H_5$ -COOC-CONHCONHC $_6H_5$ , and this with methylamine gives the desired compound.

Preparation of the Ethyl Ester of Phenyloxaluric Acid.—Five g. of oxamethane, finely powdered, was added to 10 g. of phenyl isocyanate, and heated in an open tube at 110–112° for one hour. A clear solution resulted, which solidified as it cooled to a mass still having a strong odor of phenyl isocyanate. The solid was dissolved with hot absolute alcohol and the solution filtered. A well-crystallized product separated, which weighed 4.7 g. It was recrystallized from alcohol and melted at 125–126°, with evolution of gas.

Analyses. Subs., 0.1579, 0.1958: N, 17 cc.  $(24^{\circ}, 772.1 \text{ mm.})$ ; 20.8 cc.  $(20^{\circ}, 771.4 \text{ mm.})$ . Calc. for  $C_{11}H_{12}O_4N_2$ : N, 11.87. Found: 12.19, 12.28.

OPTICAL PROPERTIES.—There were two crystalline species. A. Extinction, parallel,  $\alpha$  parallel to elongation; interference figure, biaxial; indices,  $\alpha = 1.590$ ,  $\gamma = 1.680$ . B. Extinction angle, 17–19°; birefringence, weak; indices,  $\alpha = 1.675$ ,  $\gamma = 1.755$ .

Optical Properties of Oxamethane.—Habit, large, thin, rectangular plates; extinction, parallel,  $\alpha$  parallel to elongation; interference figure, biaxial; indices,  $\alpha = 1.545 + , \gamma = 1.620$ .

Preparation of the Methylamide of Phenyloxaluric Acid.—One g. of a 33% solution of methylamine was added dropwise to 1 g. of the ethyl ester suspended in 10 cc. of water. After the resulting product had stood for half an hour, it was filtered off and dried on a tile; m. p., 210–215°; yield, 0.74 g. Phenyloxaluric acid methylamide is difficultly soluble in hot water, alcohol, acetone and chloroform. No good solvent for it was found. Microscopical examination showed that the substance was mixed with phenylurea. They could be partially separated by boiling with alcohol. The residue melted over a range of more than 5°, showing it was still not pure and the analysis indicated the same.

Analyses. Subs., 0.1383, 0.1338: N, 20.4 cc. (21°, 756.8 mm.), 24.1 cc. (25°, 759.5 mm.). Calc. for  $C_{10}H_{11}O_{3}N_{3}$ : N, 18.99. Found: 19.56, 19.96.

Optical Properties.—Extinction, parallel,  $\alpha$  parallel to elongation; indices,  $\alpha=1.595, \gamma=1.700.$ 

¹² Ref. 4c, p. 1603.

¹³ Weddige, J. prakt. Chem., 10, 196 (1874).

Phenyloxaluric acid methylamide was instantly decomposed by cold 4 N alkali. A crystalline product separated, part of which melted at 140–145° and the rest about 210°. Under the microscope it was seen to be a mixture of phenylurea and diphenylurea (impurity in the original material). Oxalic acid was found in the filtrate. The gas given off by the alkaline solution was methylamine, as it gave a chloroplatinate melting at 228–230°.

## 1,7-Dimethyl-9-phenyl-uric Acid

The starting point in the synthesis of 1,7-dimethyl-9-phenyl-uric acid is 1,7-dimethyl-uramil. It was prepared by oxidizing theobromine with potassium chlorate, reducing the product to 7-methyl-dialuric acid, and treating this with methylamine.

Preparation of 1,7-Dimethyl-9-phenyl-9-phenyl-pseudo-uric Acid.—Sixty cc. of N potassium hydroxide solution was cooled to 0°, 5 g. of finely powdered dimethyl-uramil was added, and the mixture shaken until all the solid had dissolved. A violet solution resulted. To this, 3.8 g. of phenyl isocyanate was added in small portions, and the solution shaken vigorously after each addition until it became odorless. The temperature was kept at 0-2°. The color deepened and the solution became slightly cloudy. The addition required about half an hour. The mixture was filtered, and the filtrate when acidified with dil. hydrochloric acid gave a heavy, white precipitate (8 g.); m. p., 220°. It was difficultly soluble in water, about 350 cc. of solvent being necessary to dissolve 1 g. A fine, white product was obtained, which turned pink at 160°, light yellow at 210°, and melted at 220° to an orange-red liquid. It was dried in a vacuum over sulfuric acid for analysis.

Analyses. Subs., 0.1551, 0.1533: N, 27.2 cc. (23°, 756.8 mm.), 26.9 cc. (26°, 767.5 mm.). Calc. for C₁₃H₁₄O₄N₄: N, 19.32. Found: 19.57, 19.44.

OPTICAL PROPERTIES.—Habit, small, hexagonal plates; symmetrical extinction,  $\alpha$  parallel to elongation; birefringence, strong; indices,  $\alpha = 1.555$ ,  $\gamma = 1.695$ .

Preparation of 1,7-Dimethyl-9-phenyl-uric Acid.—Five g. of the pseudo acid was dissolved in 1 liter of 20% hydrochloric acid and the solution boiled over a free flame until crystallization began. It was then evaporated on the steam-bath to 1/3 its volume, cooled and filtered. About 3 g. of material was obtained. It did not melt below 280°. The filtrate, on further evaporation, gave 0.8 g. more. The total yield was 3.8 g., or 80%. On recrystallization from water it was obtained as a fine, glistening, white powder. It was dried at 100–110° for analysis.

Analyses. Subs., 0.2796: CO₂, 0.5866; H₂O, 0.1035. Subs., 0.1460, 0.1280: N, 27.1 ec. (22°, 756.8 mm.), 23.0 ec. (21°, 765.2 mm.). Cale. for  $C_{13}H_{12}O_3N_4$ : C, 57.32; H, 4.44; N, 20.60. Found: C, 57.22; H, 4.23; N, 20.83, 20.50.

Optical Properties.—Habit, long, rectangular and hexagonal plates; extinction, symmetrical,  $\gamma$  parallel to elongation; indices,  $\alpha=1.540, \, \gamma>1.755$ .

Action of Alkali.—A solution of 0.2 g. of dimethyl-phenyl-uric acid in 12 cc. of 4 N sodium hydroxide was boiled for 10 minutes. When the solution was partly cooled and acidified, an immediate heavy precipitate of the unchanged acid, weighing 0.18 g., was obtained. It did not melt below 280°.

Methylation of 7-Methyl-9-phenyl-uric Acid.—One g. of 7-methyl-9-phenyl-uric acid was dissolved in 20 cc. of 2 N sodium hydroxide solution. Two g. of dimethyl sulfate was added, and the flask closed with a cork and shaken for 15 minutes while it was cooled with running water. A precipitate gradually separated and after 1 hour was filtered off. It weighed 0.1 g.; m. p., 258-259°. It was 1,3,7-trimethyl-9-phenyl-uric acid as a comparison of melting points and optical properties showed. When the

¹⁴ Biltz, Ber., 46, 3671 (1913).

¹⁵ Fischer, Ber., 33, 1708 (1900).

filtrate was acidified, an immediate heavy, white precipitate formed, which weighed 0.5 g. It did not melt below 280° and its optical properties were identical with those of 1,7-dimethyl-9-phenyl-uric acid.

#### Summary

- 1. The action of alkali on 1,3-dimethyl-9-phenyl-uric acid has been studied, and the course of the reaction and the nature of the decomposition products have been determined.
- 2. The primary decomposition product is 3-phenyl-isohydantoin-5-carboxylic acid methylamide. This is further decomposed by alkali to methylamine, oxalic acid, glycolic acid, formic acid and phenylurea.
- 3. Phenylisohydantoin-carboxylic acid methylamide is oxidized by hydrogen peroxide to 3-phenyl-5-hydroxyhydantoin-5-carboxylic acid methylamide, which is readily decomposed by alkali to mesoxalic acid, methylamine and phenylurea.
- 4. 1,7-Dimethyl-9-phenyl-uric acid, and the ethyl ester and methyl-amide of phenyl-oxaluric acid have been prepared for the first time and characterized.
- 5. The action of alkali on other substituted uric acids is now being investigated.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

#### DERIVATIVES OF CAMPHORONIC ACID

By Walther F. Goebel with William A. Noyes¹ Received August 25, 1923

#### Introduction

Despite the fact that camphoronic acid and many of its derivatives have been known since the latter part of the nineteenth century, no direct proof for the special structures of these derivatives has ever been brought forward. Kachler² first discovered camphoronic acid in the mother liquors of a camphor-nitric acid oxidation mixture; the true structure of the acid was first suggested by Bredt³ and later confirmed by the classical synthesis of inactive camphoronic acid by Perkin and Thorpe.⁴

Of the derivatives studied in this research there are already known one anhydro acid,  5  C₆H₁₁(CO)₂OCOOH, two isomeric anhydro acid chlorides,  6 

- ¹ An abstract of a thesis presented to the Graduate Faculty of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.
  - ² Kachler, Ann., 159, 288 (1871).
  - ³ Bredt, Ann., 292, 67 (1896).
  - ⁴ Perkin and Thorpe, J. Chem. Soc., 71, 1169 (1897).
  - ⁵ Kachler and Spitzer, Monatsh., 6, 186 (1885).
  - 6 Ref. 5, p. 193.

 $C_6H_{11}(CO)_2OCOCl$ , one diethyl ester,⁷  $C_6H_{11}(COOC_2H_5)_2COOH$ , one mono ethyl ester,⁸  $C_6H_{11}(COOC_2H_5)(COOH)_2$ , one acid imide,⁹  $C_6H_{11}(CO)_2NHCOOH$ , and two isomeric anhydrobromo acid chlorides,¹⁰  $C_6H_{10}$ -Br(CO)₂OCOCl, in which it is known that the bromine is on the primary carbon atom.

It was the original purpose of the present investigation to establish the structures of the various derivatives of camphoronic acid. The method of attack was planned as follows. If one of the anhydro acid chlorides were to be treated with anhydrous ammonia, the corresponding anhydro-amide should be formed, which on treatment with sodium hypobromite should then yield the corresponding dibasic amino acid. This compound on treatment with nitrous acid should give a dibasic hydroxy acid. If the hydroxyl group were on the primary carbon atom, trimethyl paraconic acid, a known compound would result. If it were, however, on the carbon atom bearing the two methyl groups, an isomeric lactone should result; while if the hydroxyl group were on the central carbon atom, no lactone could be produced. In this way it was hoped that the structures of the parent substances could be proved.

#### Discussion

The formation of isomeric imides, when it was desired to prepare the amides from the corresponding anhydrocamphoronyl chlorides, proved, however, to be the unavoidable obstacle presented in the outline of attack set forth above. It was shown that, from the weight of ammonia absorbed and the percentage of inorganic and organic nitrogen present, both isomeric anhydro-acid chlorides of camphoronic acid, when treated with ammonia, form an anhydro amide. The failure to obtain an indication of the reaction of the latter with sodium hypobromite to produce the corresponding amino acid may be attributed to one of two causes: either the anhydro amide actually reacted with the hypobromite according to the scheme

$$C_{6}H_{11} \stackrel{CO}{\underset{COON_{2}}{\bigcirc}} + 2NaOH = C_{6}H_{11} \stackrel{COONa}{\underset{COON_{2}}{\bigcirc}} + H_{2}O \qquad (1)$$

$$C_{6}H_{11} \stackrel{COONa}{\underset{COON_{2}}{\bigcirc}} + NaOH = C_{6}H_{11} \stackrel{COONa}{\underset{COON_{1}}{\bigcirc}} + NaOH \qquad (2)$$

$$C_{6}H_{11} \stackrel{COONa}{\underset{COON_{2}}{\bigcirc}} Br = C_{6}H_{11} \stackrel{COONa}{\underset{COON_{3}}{\bigcirc}} + NaOH \qquad (3)$$

or the anhydro amide rearranged to the more stable imidic acid structure the moment it passed into solution.

⁷ Ref. 3, p. 100.

⁸ Ref. 3, p. 104.

⁹ Hess, Ber., 28, 2689 (1895).

¹⁰ Bredt, Ann., 299, 142 (1898).

It is, of course, improbable that evidence for the above reactions can be secured. On the other hand, the unusual inactivity of both isomeric imides toward even strong alkali indicates clearly the great stability of the imide structure, while the isolation of the imide instead of the anhydro-amide on extraction of the precipitate of ammonia and anhydro acid chloride with anhydrous solvents seems to leave little doubt as to the instability of the latter compound.

The results of these researches have clearly shown the futility of an attempt at the preparation of either a dibasic amide or an anhydro amide of camphoronic acid which can be made to react with sodium hypobromite. The results, furthermore, demonstrate the necessity of covering two carboxyl groups more effectively than by forming a dimetallic salt if it is desired to prepare such a compound. The great stability of the imide seemed to indicate that a most desirable "covering group" had been found. With this in mind the attempted preparation of isomeric imide-amides from the corresponding imides was undertaken, with most gratifying results. Both imide-amides have been found to react with sodium hypobromite even in the cold, and it is through these compounds that the original plan of attack set forth in the beginning of the paper, though modified, may be brought to a satisfactory conclusion.

## Experimental Part

Preparation of Pure Camphoronic Acid.—In a 12-liter flask fitted with a condenser made from a glass tube slightly smaller than the neck of the flask, sealed at the bottom, and bearing an entrance and exit tube for water, was placed 2 kg. of camphor. was added 10 kg. of concd. nitric acid, and the mixture was gradually heated to boiling. After two weeks' continuous boiling, when the relative yield of camphoronic and camphoric acids was found to be greatest, the mixture was cooled, the camphoric acid filtered off and the mother liquor evaporated on the water-bath. The residue, which consisted of a sticky paste, was dissolved in an equal volume of hot water, the solution placed in a flask on a water-bath, and a blast of air bubbled through for two days to remove the last traces of nitric acid. (Inorganic salts, which would be formed by the neutralization of the excess of nitric acid with sodium or ammonium hydroxides, were found to inhibit materially the precipitation of barium camphoronate.) This residue was diluted with an equal volume of water and an excess of barium hydroxide, previously dissolved in water, was added. The mixture was stirred with a mechanical device and gradually heated to boiling. A cream-white, sandy precipitate of barium camphoronate resulted which was filtered off, washed, and redissolved in dil. hydrochloric acid. The solution was then boiled with 15 g. of Norite, filtered and boiled again. This was repeated eight times. The barium camphoronate was finally reprecipitated by the addition of ammonia to the neutral point, followed by boiling. Without cooling the mixture the barium salt was filtered off, washed, re-dissolved in dil. hydrochloric acid, boiled with Norite and again reprecipitated. This process was repeated four times. The final product was white barium camphoronate. The salt was again dissolved in hydrochloric acid, the barium precipitated from boiling solution by the addition of a slight excess of dil. sulfuric acid, and the filtrate evaporated to a small volume by distillation under reduced pressure. (The presence of a large excess of hydrochloric acid is desirable for it aids in the crystallization of camphoronic acid.) After standing for twelve hours the yellow mother liquors, containing about 200 g. of camphoronic acid, were filtered from 280 g. of crystalline, snow-white camphoronic acid. Recrystallization from an equal weight of water yielded fine needles melting at 164–165° when the bath was raised 1° per second from 150°. The acid in the mother liquors was recovered, after evaporation, as its barium salt.

Anhydrocamphoronic Acid was prepared in quantitative yields by heating the pure acid under reduced pressure in a distilling bulb immersed in oil at 180°. A waterwhite liquid was obtained, which solidified and then melted when the bath was raised to 133°. Recrystallization from chloroform yielded snow-white crystals melting at 139°;  $|\alpha|_{D}^{20} = +5.56$ ° (in chloroform).

Anhydrocamphoronyl Chlorides were prepared and separated by the method of Kachler and Spitzer. Instead of heating the mixture of phosphorus pentachloride and anhydrocamphoronic it was allowed to stand at room temperature. The  $\alpha$  chloride (m. p., 137–138°;  $[\alpha]_D^{20} = +6.25$ °, in chloroform) was obtained in yields of 43%. The  $\beta$  chloride (m. p., 38–39°;  $[\alpha]_D^{20} = -4.21$ °, in chloroform) was obtained in yields of 48%.

Mono-ethyl Camphoronate.—The mono-ester of camphoronic acid has been prepared hitherto only from the anhydro-ester by permitting the latter to stand with water for a considerable length of time. It has been found possible to prepare this compound by the direct esterification of the acid. Camphoronic acid was treated with 1.7 times its weight of absolute alcohol. Dry hydrogen chloride was passed in until present to the extent of 3% of the total weight of the mixture. After standing for 18 hours at room temperature the mixture was diluted and evaporated, and the crystals of mono-ester were filtered off. Recrystallization from water gave transparent crystals; m. p., 139–140°;  $[\alpha]_{0}^{20} = -30.21$ °, in absolute alcohol. The ester group in this compound is undoubtedly on the primary carboxyl group.

Analysis. Calc. for C11H18O6: C, 53.61; H, 7.37. Found: C, 53.75; H, 7.24.

The diester was separated according to the method of Bredt.⁷ Its purity was ascertained by titration;  $[\alpha]_D^{20} = -9.91^{\circ}$ , in absolute alcohol.

The Bromo-anhydrocamphoronyl Chlorides.—The preparation of these compounds was carried out exactly as Bredt¹⁰ describes, except that the bromination was catalyzed by the addition of a small amount of iron filings, followed by heating for one hour. A yield of 78% of the  $\alpha$  isomer was obtained;  $[\alpha]_0^{20} = -6.29^\circ$ , in chloroform.

Action of Ammonia and  $\alpha$ -Anhydrocamphoronyl Chloride.—In an attempt to prepare the anhydro-amide of camphoronic acid 4.85 g. of  $\alpha$ -chloride in benzene at 10° was treated with an excess of anhydrous ammonia. A precipitate resulted which, after the excess of ammonia was swept away, was filtered, dried, dissolved in water, acidified with dil. hydrochloric acid, and extracted with ether. The dried ether extract yielded 4.53 grams of solid; m. p., 196–200°. Recrystallization from hot water gave transparent crystals; m. p., 199.4–200.2°;  $[\alpha]_p = -6.86$ °, in absolute alcohol; repeated recrystallization failed to raise the melting point.

Analyses. Calc. for C9H13O4N: N, 7.03. Found: 6.99, 7.15.

Acid number. Calc. for C₆H₁₁ CO NH: 281. Found: 282.

This compound was found to be identical with the imide prepared by Hess¹¹ from the anhydro acid.

To ascertain whether the acid chloride group or the anhydride group had reacted with ammonia, 0.9670 g. of  $\alpha$  chloride was placed in a weighed bulb, dry benzene added to dissolve the chloride, the solution cooled to 10°, and anhydrous ammonia passed in

¹¹ Ref. 9. p 2687.

until no further precipitate resulted. The solvent was evaporated after the excess of ammonia was blown out with dry air, and the bulb dried to constant weight. An increase in weight of 0.1860 g. had resulted, or approximately 2.4 molecular equivalents of gas had reacted. The total percentage of nitrogen was found to be 12.05, and the ammonium nitrogen 6.80%. There was then left 5.25% of organic nitrogen. In a 1:1 mixture of anhydro amide (or acid imide) and ammonium chloride the organic nitrogen content should be 5.55%. This experiment shows conclusively that the acid chloride and not the anhydride group had reacted. The presence of 0.4 molecular equivalents' excess of ammonium nitrogen is explained by the fact that a partial rearrangement of the anhydro amide to the acid imide had occurred, which in turn reacted with more ammonia to form the ammonium salt of camphoronimide.

In the hope of securing an anhydro-amide the precipitate was placed in a dried Soxhlet thimble and extracted with anhydrous chloroform. Despite the fact that water was absent and solution resulted, rearrangement to the imide had been complete, for only an imide was recovered from the chloroform extract.

In every way the  $\beta$ -chloride behaved as did its isomer. With ammonia, however it yielded in benzene solution an imide which, hitherto, has not been prepared. The imide, on crystallization from water, yielded transparent crystals; m. p., 234.5-235°;  $[\alpha]_{p}^{20}$  = -5.40°, in absolute alcohol.

Analyses. Calc. for CoH13O4N: N, 7.03. Found: 7.01, 7.12.

Analyses. Calc. for 
$$C_0H_{10}O_4N$$
: N, 7.03. Found: 7.01, 7.12. Acid number. Calc. for  $C_0H_{11}$  CONH: 281. Found: 283.

It was hoped that the two isomeric imides could be hydrolyzed to the acid amide by alkali. Heating at 100° for 25 hours with three molecular equivalents of N potassium hydroxide produced, not hydrolysis to the amide, but a 2% hydrolysis to camphoronic acid in the case of the  $\alpha$ -imide and a 20% hydrolysis in the case of the  $\beta$ -imide.

The Action of Anhydrous Ammonia on α-Anhydrobromo-camphoronyl Chloride.— In the hope of preparing an amide of α-anhydrobromo-camphoronyl chloride the pure crystals were treated in benzene solution at 10° with an excess of dry ammonia. After the dissolved gas had been swept away the benzene was evaporated, the residue was dissolved in dil. hydrochloric acid and repeatedly extracted with ether. was obtained, which, after recrystallization from water, melted at 220°.

Analyses. Calc. for CsH12O4BrN: N, 5.03; Br, 28.76. Found: N, 5.18; Br, 28.53.

Acid number. Calc. for 
$$C_0H_{10}B_1$$
 CONH: 227. Found: 239.

The Action of Sodium Hypobromite on the Reaction Product of Anhydrous Ammonia and α- and β-Anhydrocamphoronyl Chlorides.—Experiments were carried out in which both isomeric anhydro chlorides were treated at 10° in benzene solution with dry ammonia, the excess of gas was swept away and the suspended precipitate treated with six molecular equivalents of 10% sodium hydroxide solution in which was dissolved the calculated amount of bromine. In each case, after the mixture had been heated on the water-bath for one hour, acidification with hydrochloric acid produced no evolution of carbon dioxide. An ether extraction yielded an almost quantitative recovery of the corresponding imide. The aqueous layer, after evaporation to complete dryness, gave but a trace of organic matter when extracted with absolute alcohol.

The Action of Ammonia on Mono-ethylcamphoronate. - In an attempt to prepare the mono-amide of camphoronic acid, 10 g. of an absolute alcoholic solution of mono-ester was treated with 3 molecular equivalents of dry ammonia dissolved in the same solvent. The mixture was placed in a Pyrex tube, sealed, and heated for four days at 140°. At the end of this time the tube was opened, the alcohol distilled in a vacuum, and the residue acidified and extracted with ether. A nitrogenous solid weighing 8.5 g. was obtained. Unchanged ester (0.5 g.) was dissolved from the pulverized solid with small amounts of chloroform. The residue was crystallized from hot water. A nitrogenous acidic solid was obtained; m. p.,  $199-200^{\circ}$ . This compound proved to be identical with the imide prepared from the  $\alpha$ -chloride.

The Action of Anhydrous Ammonia on Disodium Ethylcamphoronate,—A sample of  $4.82~\rm g$ . of mono-ester was heated at  $140^{\circ}$  with 1.95 molecular equivalents of sodium ethylate in a Pyrex tube for four days. A crystalline precipitate weighing  $0.90~\rm g$ , was filtered from the liquid portion at the end of the heating. This compound did not yield its nitrogen when heated with 10% alkali.

Analyses. Calc. for C6H11(CO)2NNa.COONa: N, 5.76. Found: 6.04, 5.85.

In the belief that the disodium amide was in the mother liquors, the latter were evaporated and a crystalline precipitate weighing 4.87 g. and containing 1.69% of nitrogen was obtained. When the precipitate was treated with sodium hypobromite and alkali in proper proportions, heated for one hour, cooled and acidified, no evolution of gas was observed. An ether extract yielded 4.01 g. of solid which proved to be about 25% of imide and 75% of unchanged ester.

Preparation of  $\alpha$ -Camphoronamide-imide.—A sample of  $\alpha$ -camphoronimide weighing 14.63 g. was treated with 1.2 molecular equivalents of phosphorus pentachloride. As the mixture failed to evolve hydrogen chloride, the distilling bulb containing the two substances was heated on the water-bath for an hour. At the end of this time practically all of the phosphorus pentachloride had disappeared. The phosphorus oxychloride was distilled under a vacuum. The residue, weighing 16.36 g. and consisting of a viscous yellow oil, was dissolved in absolute ether and the solution cooled to  $-20^{\circ}$ . Ligroin, at the same temperature, was added carefully. A cloud, but no crystals, appeared. One or two drops of ether were added to clear the cloud and the mixture was allowed to stand for three days at this temperature. No crystals appeared in the solution, so an excess of anhydrous ammonia was passed into the mixture. A white precipitate resulted which was filtered from the mother liquors. The latter gave only a trace of organic matter on evaporation.

The precipitate was mixed with a small amount of water and dried by suction to remove ammonium chloride. The residue was dissolved in a small amount of boiling water, the solution boiled with a little Norite, filtered, and the filtrate allowed to cool. Transparent crystals were obtained; m. p.,  $235-236^{\circ}$ ;  $[\alpha]_{541.6}^{280} \mu\mu = +11.87^{\circ}$ , in absolute methyl alcohol.

Analysis. Calc. for C9H14O2N2: N, 14.13. Found: 13.89.

Preparation of the Acid Chloride of  $\beta$ -Camphoronimide.—To 12.02 g. of  $\beta$ -camphoronimide, in a small distilling bulb, was added 1.2 molecular equivalents of pulverized phosphorus pentachloride, and the mixture warmed on the water-bath for one hour. At the end of this time glistening crystals, quite unlike the imide, precipitated from the mixture as it cooled. After distillation of the phosphorus oxychloride under a vacuum, the residue, weighing 14.3 g., was washed well with absolute ether; 11 g. of solid was obtained. This compound, on analysis, proved to be the acid chloride of the  $\beta$  imide. It was found to be very soluble in chloroform and in hot benzene. When recrystallized from the latter a beautiful solid product was obtained; m. p., 175.5–176.5°;  $\alpha$ 16.1°  $\alpha$ 16.1°  $\alpha$ 16.1°  $\alpha$ 17.6°  $\alpha$ 18.32°, in chloroform.

Analyses. Calc. for C₉H₁₂O₃NC1: N, 6.43; Cl, 16.31. Found: N, 6.18; Cl, 16.20.

Preparation of  $\beta$ -Camphoronimide-amide.—An excess of anhydrous ammonia was passed into a chloroform solution of 5.2 g. of the  $\beta$ -imide acid chloride, the excess of gas was swept away, the solvent evaporated, and the solid precipitate washed with a

small amount of water to remove ammonium chloride. The residue was dissolved in boiling water, the solution filtered and allowed to cool. Transparent crystals of the  $\beta$ -imide-amide were obtained; in. p., 205°;  $[\alpha]_{541.6\mu\mu}^{1289} = -13.73$ °, in absolute acetone.

Analysis. Calc. for C9H14O3N2: N, 14.13. Found: 13.95.

# Summary

- 1. Anhydrocamphoronic acid has been prepared in quantitative yields.
- 2. Mono-ethyl camphoronate has been prepared by the direct esterification of the acid in yields of 50%.
- 3. Monomethyl camphoronate yields an imide on treatment with ammonia at 140°. This imide is identical with that obtained from the anhydro acid under similar treatment.
- 4. Anhydrous ammonia reacts with  $\alpha$ -anhydrocamphoronyl chloride to yield first an anhydro amide and then an acid imide by rearrangement. This imide is identical with that obtained from the mono-ester.
- 5. Anhydrous ammonia reacts with  $\beta$ -anhydrocamphoronyl chloride in a similar manner to form an isomeric imide. This compound is new in the camphoronic acid series.
- 6. Anhydrous ammonia reacts with bromo-anhydrocamphoronyl chloride to form a bromo-imide. This compound is new in the camphoronic acid series.
- 7. Potassium hydroxide fails to open the ring of either  $\alpha$  or  $\beta$ -camphoronimide to yield a dibasic amide. In each case partial hydrolysis to the parent acid is the only reaction involved.
- 8. When the reaction product of anhydrous ammonia and  $\alpha$ -anhydrocamphoronyl chloride, or  $\beta$ -anhydrocamphoronyl chloride, or disodium ethylcamphoronate is treated with sodium hypobromite the corresponding amino acid is not formed. In each case an imide is produced.
- 9. When  $\alpha$ -camphoronimide is treated first with phosphorus pentachloride and then with anhydrous ammonia an imide-amide of camphoronic acid is produced. This compound is new in the camphoronic acid series. The compound reacts readily with sodium hypobromite.
- 10. The acid chloride of  $\beta$ -camphoronimide has been prepared. This compound is new in the camphoronic acid series.
- 11. When the acid chloride of  $\beta$ -camphoronimide is treated with anhydrous ammonia an amide is formed. This amide is isomeric with that prepared from the  $\alpha$ -imide, is new in the camphoronic acid series, and reacts readily with sodium hypobromite.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY]

# STUDIES IN THE DIPHENIC ACID AND IN THE FLUORENONE SERIES. I

By H. W. Underwood, Jr., and E. L. Kochmann¹
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Phenolphthalein, fluorescein and gallein are prepared by well-known methods which involve the condensation of phthalic anhydride with phenol, resorcinol and pyrogallol, respectively. A part of this paper

is an account of results obtained by using diphenic anhydride,  $\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$ 

and allied compounds in place of phthalic anhydride in these processes. Sulfuric acid is frequently employed as a condensing agent in the synthesis of fluorescein. On account of the fact that sulfuric acid transforms diphenic anhydride into the isomeric diphenyleneketone-4-carboxylic acid,  $C_6H_4$ 

 $C_6H_3$ — $C_9H$ 

chloride as dehydrating agents in our work. Equations for the condensations with phenol and with resorcinol might be written as follows:

The crystalline substance obtained from the phenol reaction did not give a red solution when it was dissolved in caustic alkali, nor did the sodium salt of the crystalline compound isolated from the resorcinol-anhydride condensation show fluorescence in solution. However, the amorphous residue from Reaction 1 behaved like phenolphthalein and that from Reaction 2 showed properties similar to those of fluorescein. Consideration of these results caused us to believe that the dehydrating agents employed might have changed a part of the diphenic anhydride into diphenyleneketone-4-carboxylic acid and that the ketone oxygen of the latter had reacted with two atoms of ring hydrogen from two molecules of phenol

¹ The experimental results described in this paper are taken from a thesis submitted to the Faculty of the Massachusetts Institute of Technology by E. L. Kochmann in partial fulfillment of the requirements for the degree of Bachelor of Science.

or of resorcinol to yield substances respectively colored or fluorescent in alkaline solution. The formula for the sodium salt of the phenol reac-

Experiments were carried out to test the validity of these ideas. It is customary to explain the red color of phenolphthalein in alkaline solution by saying that a quinoid ring is formed; this phenomenon is also said to be involved in salt formation by fluorescein. If salts having formulas analogous to that given above are responsible for the color and fluorescence obtained in our experiments, then we have instances of indicator effects and of fluorescence which do not involve quinoid ring formation. To secure further evidence on this point, we have condensed fluorenone with phenol and with resorcinol² on the supposition that the oxygen atom in this ketone would unite with two atoms of ring hydrogen from two molecules of phenol or of resorcinol. The remainder of our research consists of an investigation of the value of the bromine derivative of the resorcinol-diphenyleneketone-4-carboxylic acid compound and of the pyrogallol-diphenic anhydride condensation product as dyes.

After a considerable part of this work had been completed two articles which mentioned reactions of diphenic anhydride were published. Dutt³ described phenoldiphenein and resorcinoldiphenein and Bischoff and Adkins⁴ dealt with the latter as well as the reaction between diphenylene-ketone-4-carboxylic acid and resorcinol. Apparently all of these investigators ascribe the production of color and fluorescence in alkaline solutions to the diphenic anhydride condensation products, and they do not touch upon the transformation of diphenic anhydride into the isomeric ketone acid by the condensing agents they employed. The differences between our results and those obtained by Dutt and by Bischoff and Adkins with regard to this matter, and in other respects, are brought out in the description of our experiments and in the summary of this paper.

# Discussion of Experiments

All of the temperatures given below are uncorrected.

Diphenic Anhydride.—In order to ascertain whether diphenic acid could be transformed into the anhydride by heat, samples of the material were maintained at temperatures 10° above its melting point for half

² Experiments involving some of these reactions of fluorenone and of diphenylene-ketone-4-carboxylic acid were performed long ago by Graebe and Aubin [Ann., 247, 257 (1888)].

³ Dutt, J. Chem. Soc., 123, 225 (1923).

⁴ Bischoff and Adkins, This Journal, 45, 1030 (1923).

an hour. Examination of the product showed that no diphenic anhydride had been formed.

Subsequently, the following procedure was adopted.

Mixtures of diphenic acid, acetic anhydride and glacial acetic acid (solvent) were heated at  $145^{\circ}$ , then allowed to cool, the crystalline solid was collected on a filter and the filtrate poured into water in order to obtain any material held in solution. All of the solid reaction products were treated with a cold 20% solution of sodium carbonate to remove diphenic acid. Results are given below.

Diphenic acid G.	Acetic anhydride G.	Calc. amt. X	Acetic acid G.	Time of heating hours	Diphenic anhydride G.	Vield
10	20	4.8	20	0.50	8.7	94.0
25	50	4.8	50	1.25	21.5	92.9
25	11.5	1.1	45	1.25	18.5	79.9
15	9.4	1.5	27	1.00	12.1	87.1
15	12.6	2.0	27	1.00	12.2	87.9
15	15.7	2.5	25	1.00	12.65	91.1
30	31.4	2.5	50	2.00	24.7	89.0

These experiments produced diphenic anhydride which melted at 222-224°.

Phenol and Diphenic Anhydride.—Twenty-one g. of phenol (calc. amt. × 2.7), 10 g. of diphenic anhydride and 16 g. of fuming stannic chloride were placed in a round-bottom flask provided with an air condenser and heated at 130-135° for 15 hours. Steam distillation was employed to remove excess of phenol. The solid reaction product was collected on a filter, dried and finely powdered. Treatment with (1) a 50% solution of sodium bicarbonate showed that none of the condensation product was soluble in this medium. Repeated extractions with (2) ammonium hydroxide, with (3) sodium carbonate solution and with (4) 3 N sodium hydroxide solution followed by acidification of the extract liquors and washing and drying of the precipitates thereby produced, gave amorphous brown or cream-colored powders having the following weights: (2) 11.56 g., (3) 0. g., (4) 2.9 g. The ammonium hydroxide used in these extractions was prepared by mixing equal volumes of material having a density of 0.90 and water; the sodium carbonate solution was 50%. Solutions of these concentrations and others given above were employed in all of the experiments described in this paper. When the several alkaline liquids were made acid, the solids formed as gelatinous precipitates which held inorganic salts very tenaciously. It was necessary to grind the dried powders repeatedly with water in order to remove the sodium chloride which was mixed with them. By the use of glacial acetic acid as a solvent, colorless rhombic crystals (m. p., 250-251°) were obtained from the portion of the condensation product soluble in ammonium hydroxide; 2.7 g. of crystals was obtained from 5 g. of crude material. These crystals gave a yellow solution in sodium hydroxide, but the amorphous powder produced by dilution of the acetic acid filtrate dissolved in aqueous sodium hydroxide with a deep red color. Dutt3 described phenoldiphenein as pinkish white needles (from dil. alcohol, m. p., 134°, containing 2 molecules of water of crystallization) which dissolved in sodium hydroxide solution with a reddish-pink color.

Analyses (crystals, m. p., 250-251°). Calc. for C₂₆H₁₈O₄: C, 79.16; H, 4.60. Found: C, 78.74, 78.80; H, 5.02, 5.09.

We intend to investigate the acetyl derivative of phenoldiphenein; preliminary experiments indicate that it is insoluble in cold caustic alkali solutions.

Resorcinol and Diphenic Anhydride.—Twenty g. of fused and finely divided zinc chloride was gradually added to a mixture of 25 g. of resorcinol (calc. amt. × 1.27) and 20 g. of diphenic anhydride stirred and maintained at 175°. The total time of heating was 4 hours. After the dark red melt had cooled, it was powdered, boiled with dil. hydrochloric acid, drained on a filter and dried. It was then washed thoroughly with water, treated with a 50% solution of sodium hydroxide and the undissolved material collected on a filter. Acidification of the alkaline liquid yielded a brown precipitate which weighed 25.5 g, when washed and dried. To an almost neutral solution of this material in aqueous sodium hydroxide an excess of lead acetate solution was added and the lead lake thereby produced was removed by filtration. After drying the latter, it The finely powdered lead compound was suspended in alcohol and weighed 50.4 g. treated with an excess of hydrogen sulfide. After removal of the lead sulfide, the alcoholic solution of the condensation product was evaporated to dryness or diluted with water to obtain the crude resorcinoldiphenein which came down as a reddish-brown powder (weight when dry, 22 g.). A filtered solution of the latter in hot alcohol was carefully diluted with water until a slight precipitate appeared, and then warmed and allowed to stand. Almost colorless crystals were thereby obtained, which melted at 178-179° when dry; 1.9 g. of crystals was secured from 5 g. of crude material. These crystals dissolved in sodium hydroxide solution to yield a yellow liquid with practically no fluorescence. The brown, amorphous powder obtained by concentration of the alcoholic solution gave a strongly fluorescent solution when dissolved in aqueous sodium hydroxide.

According to statements made by Dutt,³ resorcinoldiphenein forms brown prisms (from dil. alcohol), m. p., 172°, which show a brilliant green fluorescence when dissolved in caustic alkalies. He gave the formula as  $C_{26}H_{16}O_5$ . Although Bischoff and Adkins⁴ did not report a quantitative analysis of resorcinoldiphenein for carbon and hydrogen, they concluded from a determination of the metal content of the sodium salt, which they write as  $C_{26}H_{14}O_5Na_4$ , that the oxygen bridge present in the original compound is opened by dissolving the material in sodium hydroxide solution.

Analyses (crystals, m. p., 178-179°). Calc. for C₂₆H₁₈O₆: C, 73.22; H, 4.25. Found: C, 72.94, 73.00; H, 4.55, 4.45.

Pyrogallol and Diphenic Anhydride.—A mixture of 7 g. of pyrogallol (calc. amt. × 1.25), 5 g. of diphenic anhydride and 8 g. of fuming stannic chloride was heated at 125–130° for 7 hours. The mass was cooled and diluted with water. Subsequent treatment of the product was the same as that employed in the case of the phenol condensation, except that the steam distillation was omitted. Yields were as follows: none of the material was soluble in (1) sodium bicarbonate or in (2) ammonium hydroxide; (3) sodium carbonate extract, 4.2 g. of a black powder; (4) sodium hydroxide extract, 4.4 g. of a black powder. None of these materials melted at 325°, and they were practically insoluble in all of the usual organic solvents as well as nitrobenzene, aniline and quinoline. We did not succeed in getting these substances pure enough for accurate analyses.

Diphenyleneketone-4-carboxylic Acid from Diphenic Anhydride.—Five g. of diphenic anhydride and 7 g. of anhydrous stannic chloride were heated at 120–130° for 7 hours. The cold reaction product was poured into water, filtered and washed. It was found to be completely soluble in a 50% solution of sodium carbonate. When the latter was acidified, it yielded a yellow precipitate. This was identified as diphenyleneketone-4-carboxylic acid by a mixed-melting-point with some of the ketone acid prepared by treating diphenic acid with sulfuric acid.⁵ Evidently the stannic chloride transformed all the diphenic anhydride into the isomeric diphenyleneketone-4-carboxylic acid.

⁵ Graebe and Mensching, Ber., 13, 1302 (1880).

Similar results were obtained by maintaining a mixture of 5 g. of diphenic anhydride and 4 g. of anhydrous zine chloride at 225° for 8 hours.

Diphenic Anhydride from Diphenyleneketone-4-carboxylic Acid.—A mixture of 5 g. of diphenyleneketone-4-carboxylic acid, 10 g. of acetic anhydride and 5 cc. of glacial acetic acid was heated at  $140-150^{\circ}$  for 6 hours. The solid reaction product obtained when this mixture was cooled, diluted with water and filtered, was treated twice with a 50% solution of sodium carbonate. The undissolved residue upon recrystallization from benzene formed needles (0.9 g.) which melted at  $222^{\circ}$ . This was identified as diphenic anhydride by a mixed-melting-point with some anhydride of known purity. Apparently diphenyleneketone-4-carboxylic acid can be changed into diphenic anhydride, but the process is very slow.

Phenol and Diphenyleneketone-4-carboxylic Acid.—A mixture of 10 g. of phenol, 5 g. of diphenyleneketone-4-carboxylic acid and 8 g. of fuming stannic chloride was maintained at 120–125° for 5 hours. Subsequent treatment of the product was the same as that employed in the case of phenoldiphenein. Yields were as follows: none of the product dissolved in (1) sodium bicarbonate solution or in (3) sodium carbonate solution; (2) ammonium hydroxide extract, 4.5 g. of a salmon-red powder (m. p., 180–185°); (4) sodium hydroxide extract, 1.05 g. of reddish-brown material (m. p., 213–220°).

Analyses. Calc. for  $C_{20}H_{18}O_4$ : C, 79.16; H, 4.60. Found: C, 78.63, 78.70; H, 5.1, 5.13.

Resorcinol and Diphenyleneketone-4-carboxylic Acid.—A mixture of 7 g. of resorcinol (calc. amt. × 1.4), 5 g. of diphenyleneketone-4-carboxylic acid and 18 g. of fuming stannic chloride was heated for 10 hours at 120–130°. The method used for working up the reaction mass was similar to that already described for the phenol-diphenic anhydride condensation product. The yields were: (1) sodium bicarbonate extract, 1.3 g. of an amorphous substance (m. p., 215–240°); (2) material soluble in ammonium hydroxide, 6.7 g. (did not melt at 325°); (3) sodium carbonate extract, 0 g.; (4) a substance removed by sodium hydroxide solution, 0.5 g. (this remained solid at 325°). All of these materials were brown or red amorphous powders which gave a deep green fluorescence when dissolved in caustic alkali solution. Analyses were made of samples obtained directly from the reaction product by treatment with sodium hydroxide solution. The material was subsequently dissolved in alcohol, filtered and the alcohol-soluble portion obtained by dilution with water; this treatment was repeated several times.

Analyses.⁶ Calc. for C₂₆H₁₈O₆: C, 73.22; H, 4.25. Found: C, 72.87, 72.79; H, 4.61, 4.7.

It is planned to investigate the acetyl derivatives of this condensation product as well as the one obtained from phenol; preliminary experiments indicate that the acetyl compounds are soluble in cold sodium hydroxide solution.

Phenol and Fluorenone.—In an Erlenmeyer flask 3.5 g. of fluorenone and 5.5 g. of phenol (50% excess) were mixed with 9 g. of fuming stannic chloride, and the whole was then heated at  $130-140^{\circ}$  for 6 hours. After cooling the mass, it was steam distilled to

⁶ It was found impossible to burn this compound, as well as several others produced in our work, in ordinary combustion tubing. Consequently, for all the carbon-hydrogen determinations mentioned in this paper we used tubes made of fused silica, mixed the compounds intimately with fine copper oxide and burned them in a current of oxygen during the course of 8 to 10 hours. Special precautions were taken with regard to the hygroscopicity of fine copper oxide, and in some cases hydrogen was determined separately. Every compound analyzed was previously dried at 110° to constant weight.

remove excess of phenol, then filtered and treated with 3 N sodium hydroxide solution. When the latter was acidified a salmon-red precipitate was obtained which weighed 4.1 g. after it had been washed and dried, and melted incompletely at 241–243°. This substance dissolves in sodium hydroxide and forms a deep red solution. A portion was several times dissolved in hot alcohol, separated from impurities by filtration and recovered by dilution of the alcoholic solution with water. This material was analyzed.

Analyses. Calc. for  $C_{28}H_{18}O_2$ : C, 85.68; H, 5.17. Found: C, 85.27, 85.35; H, 5.50, 5.56.

Resorcinol and Fluorenone.—Three and one-half g. of fluorenone, 5.4 g. of resorcinol (25% excess) and 9 g. of anhydrous stannic chloride were heated together at 130–140° for 6 hours. The reaction product was treated by a procedure similar to that used in the case of the phenol-fluorenone condensation, except that the steam distillation was omitted. One g. of a brown powder was thereby obtained, and 5.0 g. of the crude material was found to be insoluble in sodium hydroxide solution. This brown powder showed a strong fluorescence in alkaline solution. It was prepared for analysis by treatment with alcohol as already described in the account of the previous experiment.

Analyses. Calc. for C₂₅H₁₈O₄: C, 78.51; H, 4.74. Found: C, 78.12, 78.20; H, 5.10, 5.3.

Bromination of Resorcinol Condensation Products.—One g. of the crystalline resorcinoldiphenein was dissolved in 15 cc. of hot alcohol, the solution placed in an Erlenmeyer flask provided with a reflux water condenser and then 4 g. of bromine (calc. amt.  $\times$  2.7) was added to the boiling solution during the course of an hour. Yellow rhombic crystals soon appeared in the liquid. At the completion of the reaction these were collected and dried. They melted at 273° and weighed 1.2 g. When dissolved in sodium hydroxide solution, the bromine compound gave a yellow solution which showed no fluorescence. If the bromine is added quickly to the hot alcoholic solution or to a cold one, the product is an amorphous powder.

Analyses (crystals dried at 110°). Calc. for  $C_{26}H_{14}O_6Br_4$ : Br, 43.08. Found: 42.90, 42.95.

One g. of the part of the resorcinol-diphenyleneketone-4-carboxylic acid condensation product which was soluble in ammonium hydroxide was brominated in a similar way. Filtration of the cold reaction mixture yielded a brownish-red, amorphous powder which weighed 0.8 g. when washed and dried. It did not melt at 325°, and dissolved in sodium hydroxide solution with the development of a deep red color. This powder was dissolved in a mixture of acetone and alcohol, separated from impurities by filtration and recovered by evaporation of the solvents. Determinations of the bromine content of a sample prepared in this way gave results which were several per cent. below that calculated for the tetrabromo derivative, and which indicated the presence of some dibromo compound or other impurities.

Dyeing Experiments.—A sample of skein silk and one of woolen yarn were worked for half an hour in slightly acid baths containing 3% (based on weight of silk or wool) of the sodium salt of the bromine derivative of the resorcinol-diphenyleneketone-4-carboxylic acid condensation product. The wool was dyed a very light pink, and the silk acquired a flesh color. Parallel experiments in which eosin was used in place of the keto acid derivative gave the usual results.

One gram of woolen yarn previously mordanted with potassium dichromate solution was stirred for an hour in a slightly acid, hot aqueous suspension of 0.4 g. of freshly precipitated and washed pyrogalloldiphenein. After the wool was washed it showed a very slight brown coloration.

# Summary

From the reaction product obtained by condensing phenol with diphenic anhydride in the presence of fuming stannic chloride a crystalline compound, phenoldiphenein, can be obtained. This dissolves in sodium hydroxide solution with development of a yellow color. Crystalline resorcinoldiphenein has been isolated from the crude material secured by heating resorcinol and diphenic anhydride together with the use of fused zinc chloride as a dehydrating agent. Resorcinol-diphenein gives a yellow solution with sodium hydroxide, but does not show fluorescence. The appearance of the solutions of the sodium salts of these compounds is strange in view of the fact that they are similar to phenolphthalein and to fluorescein in structure. The statements made by Dutt and by Bischoff and Adkins as to the constitution and properties of phenoldiphenein and resorcinoldiphenein appear to be in error.

The amorphous condensation product of phenol and diphenyleneke-tone-4-carboxylic acid has been secured by heating these two compounds together and also from the residues left after the removal of the crystal-line compound obtained by the reaction between phenol and diphenic anhydride. The presence of the ketone acid derivative here is apparently due to the transformation of a part of the diphenic anhydride into the isomeric diphenyleneketone-4-carboxylic acid by the action of fuming stannic chloride. This amorphous condensation product dissolves in sodium hydroxide solution with development of a deep red color. Similarly crude resorcinoldiphenein was found to contain the ketone acid-resorcinol product. The latter has also been prepared directly from diphenyleneketone-4-carboxylic acid.

One molecule of fluorenone reacts with two of phenol or of resorcinol to give condensation products which show, respectively, a red color and a green fluorescence in alkaline solutions. Apparently, these compounds, as well as those obtained from diphenyleneketone-4-carboxylic acid, are examples of substances which show indicator effects and fluorescence without the formation of a quinoid ring.

As dyes, the bromine derivatives of resorcinoldiphenein and of the ketone acid-resorcinol condensation product as well as pyrogalloldiphenein have little or no value.

Cambridge 39, Massachusetts

[Contribution from the Chemical Laboratory of Clark University, No. I, 33]

# STUDIES RELATING TO METALLO-ORGANIC COMPOUNDS. III. COMPOUNDS FORMED BETWEEN ALKYL TIN HALIDES AND AMMONIA AND THE AMINES

By Charles A. Kraus and Willard N. Greer Received September 10, 1923

It is known that ammonia, as well as certain of the amines, combines with metallo-organic compounds of the type  $M^nR_{n-1}X$ , where M is a metal of normal valence n, R is a univalent organic group, and X is a strongly electronegative element or group of elements. Compounds of this type have been studied in particular by Werner and Pfeiffer, 1 and the results have been interpreted in terms of Werner's theory. The physical-chemical properties of the different compounds formed by the metallo-organic halides with ammonia and the amines have led us to infer a different constitution. The trimethyl tin group, like other groups of the same type, of the general formula  $M^nR_{n-1}$ , closely resembles hydrogen or the methyl group in its properties. These groups exhibit a marked tendency to add to ammonia or the amines to form compounds of the ammonium type, in which the metallo-organic group is directly attached to nitrogen. The analogy between trimethyl tin iodide and methyl iodide, for example, is complete in this respect. Both add to a tertiary amine, such as pyridine, to form compounds of relatively high melting points, which, in the pure state as well as in solution, exhibit marked electrolytic properties. is to be anticipated that these compounds in the liquid mixture will not be entirely stable; that is, in a mixture of the two components, the meltingpoint curve will exhibit a rounded maximum. While, however, methyl iodide does not add to ammonia or the primary or secondary amines readily under ordinary conditions, trimethyl tin iodide, as well as the other halides of the same group, adds readily to ammonia, the primary and secondary amines, as well as to the tertiary amines, to form compounds of the ammonium type. The group, therefore, resembles hydrogen perhaps somewhat more closely than it does the methyl group.

This behavior on the part of the metallo-organic compounds of this class is not restricted to compounds of tin but probably holds generally, although thus far only tin and mercury compounds have been investigated. It is true, however, that silicon exhibits a similar behavior, triphenyl silicyl chloride combining with one molecule of ammonia to form a compound. Carbon also exhibits this same property. This is shown in a striking manner by those compounds of carbon in which the central carbon atom has approximately the same affinity for the negative electron as have the corresponding metallo-organic groups. Carbon groups of this type are

Werner and Pfeiffer, Z. anorg. Chem., 17, 82 (1898).

found among the compounds of the triphenylmethyl type. Triphenylmethyl chloride, for example, adds a molecule of ammonia to form a comparatively stable compound.

It appeared of interest to investigate the compounds formed in a number of cases. In particular, it appeared of importance to investigate certain of the tin compounds, inasmuch as Werner and Pfeiffer concluded that two molecules of ammonia or an amine were added in the case of these compounds. Thus they found that triethyl tin iodide takes up two molecules of aniline, while the literature indicates that triethyl tin iodide also takes up two molecules of ammonia.

In determining the number of molecules of amine combined with the metallo-organic halide, in general, a determination of the halogen content of the compound was made. These analyses usually checked closely and sufficed to distinguish between one and two molecules of the amine in the compound. In the case of ammonia, however, direct determination of the ammonia was likewise made. In cases where results seemed doubtful, a rough determination of the melting-point curve of mixtures of the constituents was made.

# **Experimental Part**

Trimethyl Tin Chloride and Ammonia.—Trimethyl tin chloride was prepared by treating tetramethyl tin with chlorine in an ice bath with the exclusion of light. The chloride was purified by distillation and finally by recrystallization from petroleum ether at low temperatures.

Trimethyl tin chloride is readily soluble in all types of solvents. The ammonia complex, however, is soluble only in solvents which are capable of dissolving typical salts. The compound does not melt but sublimes at higher temperatures at ordinary pressures.

Trimethyl tin chloride was introduced into a glass tube provided with suitable stopcocks and arranged so that it could be weighed. Ammonia was passed over the compound at ordinary temperatures and pressures after which the ammonia absorbed was determined by weighing, a correction being made for ammonia in the vapor state.

Subs., 0.7384: NH₃ absorbed, 0.0574. Calc. 1 mol. of NH₃, 7.87. Found: 7.77. Trimethyl tin chloride was placed in a tube and ammonia condensed in the same at liquid ammonia temperatures, until all the compound was in solution. The excess of ammonia was then evaporated and finally pumped off for a short time.

Subs., 0.1707, 0.2639: AgCl, 0.1100, 0.1751. Calc. for 1 mol. of ammonia: Cl, 16.40; calc. for 2 mols.: 15.20. Found: 15.94, 16.41.

It is probable that under these conditions the compound takes up two molecules of ammonia, one molecule of which, however, is apparently not firmly held.

A sample of the same material was again placed on the pump and exhausted for two hours, and analyses made as before.

Subs., 0.3426, 0.3823: AgCl, 0.2280, 0.2557. Found: Cl, 16.46, 16.55.

These results show clearly that while trimethyl tin chloride probably takes up two molecules of ammonia, only one molecule is firmly held.

Trimethyl Tin Chloride and Aniline.—Trimethyl tin chloride was dissolved in petroleum ether and aniline added. A solid precipitate was formed which was thrown on the filter, washed with ether and then dried.

Subs., 0.5254, 0.6144: AgCl, 0.2559, 0.3028. Calc. for 1 mol. of aniline: Cl, 12.13. Found: 12.04, 12.19.

The melting-point curve of mixtures of trimethyl tin chloride and aniline was examined. An equimolar mixture solidified homogeneously at 84.5°. With 1.5 mols. of aniline per mol. of chloride initial precipitation took place at 72°. With two mols. of aniline per mol. of chloride the mixture remained liquid at room temperatures.

It is evident that trimethyl tin chloride combines with one molecule of aniline.

Trimethyl Tin Chloride and Pyridine.—Trimethyl tin chloride was treated with pyridine in petroleum ether solution. A white product precipitated at 0° which was washed with petroleum ether and dried; m. p., 37°.

Subs., 0.2522, 0.2668: AgCl, 0.1303, 0.1383. Calc. for 1 mol. of pyridine: Cl, 12.74. Found: 12.78, 12.82.

Trimethyl tin chloride and pyridine combine in equimolar proportions.

Trimethyl Tin Iodide and Ammonia.—A sample of trimethyl tin iodide was dissolved in ammonia, the excess of solvent was evaporated, and the residual vapor removed by connecting to a vacuum pump for a few minutes. The compound was then analyzed for iodine.

Subs., 0.1784, 0.2542: AgI, 0.1326, 0.1910. Calc. for 1 mol. NH₃: I, 41.24; calc. for 2 mols. NH₃: 39.08. Found: 40.18, 40.62.

A sample of the same material was then placed on the pump for a period of one hour, after which it was analyzed.

Subs., 0.3565, 0.5784: AgI, 0.2716, 0.4442. Found: I, 41.18, 41.51.

A sample of the iodide was dissolved in ether and a stream of ammonia gas passed through the solution. The compound precipitated from solution and was washed with ether and dried.

Subs., 0.1867, 0.2076: AgI, 0.1374, 0.1518. Found: I, 39.78, 39.53.

Trimethyl tin iodide evidently combines with two molecules of ammonia, one of which is lost readily, as is indicated by the fact that the sample which was subjected to the action of the pump for only a short period still yielded iodine values intermediate between those for compounds containing one and two molecules of ammonia, respectively. On

the other hand, the iodine content of the compound which was precipitated from ether solution and not subjected to the action of the pump corresponds fairly closely to that of a compound containing two molecules of ammonia.

Trimethyl Tin Iodide and Aniline.—The freezing-point curves of various mixtures of trimethyl tin iodide and aniline were determined. In Table I are given the temperatures at which initial precipitation occurred.

Table I
Freezing-point Data for Mixtures of Trimethyl Tin Iodide and Aniline

Molper cent. aniline	Initial temperature of precipitation °C.	Molper cent. aniline	Initial temperature of precipitation °C.
6.88	52	66.65	95.2
20.11	77	72.22	94.5
34.21	88	76.2	93
50.77	93.5	78.96	92
60.84	95	81.83	90.7

It is evident that trimethyl tin iodide and aniline form a compound containing two molecules of aniline which melts homogeneously at 95.2°. The melting-point curve is extremely flat, which indicates that the compound is comparatively unstable.

Trimethyl Tin Iodide and Pyridine.—An equimolar mixture of trimethyl tin iodide and pyridine was found to melt at 60.5°, the temperature remaining constant until complete solidification had taken place. The further addition of one-half molecular equivalent of pyridine lowered the initial point appreciably, while with the addition of two molecular equivalents of pyridine the initial point of precipitation was lowered to 55°. The mixture was still mushy at room temperatures. Trimethyl tin iodide and pyridine combine in equimolar proportions.

Triethyl Tin Iodide and Pyridine.—Werner and Pfeiffer were unable to obtain a solid precipitate from mixtures of triethyl tin iodide and pyridine. Accordingly, mixtures of these two constituents were subjected to lower temperatures and the course of the melting-point curve approximated. With 40 mol.-per cent. of pyridine the mixture was still soft at —30°. With 50 mol.-per cent. of pyridine the mixture solidified homogeneously at —17°. On further addition of pyridine the melting point was lowered. The mixture containing 66 mol.-per cent. of pyridine still contained liquid at —30°. Trimethyl tin iodide remains liquid at —36°.

Trimethyl tin iodide and pyridine thus form a compound in equimolar proportions which solidifies homogeneously at —17°. This accounts for the failure of Werner and Pfeiffer to establish the formation of a compound.

Dimethyl Tin Dichloride and Pyridine.—The dichloride was dissolved in alcohol and pyridine added, a white precipitate being formed. This

product after washing and drying was found to sublime at a temperature of 145°.

Subs., 0.1321, 0.1578: AgCl, 0.0999, 0.1197. Calc. for 2 mols. of pyridine: Cl, 18.77. Found: 18.71, 18.76.

Evidently one molecule of pyridine is added for each equivalent of chlorine present in the molecule of dimethyl tin dichloride.

Ethyl Mercuric Chloride and Ammonia.—A sample of ethyl mercuric chloride was treated with liquid ammonia in a weighing tube. The excess ammonia was evaporated and the last traces removed by means of a pump.

Subs., 1.4408:  $NH_3$  absorbed, 0.0940. Calc. for 1 mol. of  $NH_3$ :  $NH_3$ , 6.04. Found: 6.12.

Ethyl mercuric chloride and ammonia combine in equimolar proportions. Amyl Mercuric Iodide and Ammonia.—A sample of amyl mercuric iodide was treated with liquid ammonia in a weighing tube and the amount of ammonia absorbed determined by weight after pumping off the excess.

Subs., 0.7282: NH $_3$  absorbed, 0.0288. Calc. for 1 mol. of NH $_3$ : NH $_3$ , 4.10. Found: 3.8.

Amyl mercuric iodide and ammonia combine in equimolar proportions.

When ethyl mercuric chloride and amyl mercuric iodide were treated with triethylamine and with pyridine, compounds were precipitated at 0°. These, however, melted or dissolved when room temperatures were reached and were not investigated further.

#### Discussion

Werner and Pfeiffer attempted to account for the compounds of the trimethyl tin halides with ammonia and the amines on the basis of Werner's theory. They expected to find these compounds combining with two molecules of ammonia or the amines, and indeed they found that in the case of triethyl tin iodide and aniline two molecules of aniline combined with a molecule of the iodide. The results above presented, however, indicate that it is the exception that a trimethyl tin halide combines with two molecules of an amine. Furthermore, in the case of a compound with ammonia, in which instance two molecules are combined with trimethyl tin iodide, one molecule of ammonia is held very loosely while the second molecule is held extremely tenaciously. It is interesting, too, to note that the alkyl mercury halides combine only with a single molecule of ammonia or the amines.

To account for the combination of ammonia and the amines with the alkyl tin halides it appears more rational to assume that the alkyl tin group migrates to the nitrogen atom, yielding pentavalent nitrogen and consequently a compound of the ammonium type. In this case the compound should have the properties of a salt, in view of the known properties of

pentavalent nitrogen in the ammonium group. The reaction is entirely similar to that taking place between methyl iodide, for example, and pyridine, in which case reaction takes place according to the following equation:  $CH_3I + C_6H_5N = C_6H_5NCH_3I$ . In the case of trimethyl tin iodide, reaction takes place according to the equation:  $(CH_3)_3SnI + C_6H_5N = C_6H_5NSn(CH_3)_3I$ .

This view of the constitution of the compounds formed between the alkyl metal halides and ammonia and its derivatives is in agreement with the properties of the resulting compounds; more particularly, it serves to account for the fact that solutions of the alkyl metal halides in the amines conduct the current with considerable facility, while solutions of the same substances in solvents of the non-basic type are virtually non-conductors.

The alkyl metal groups, such as the trimethyl tin group, have a very marked affinity both for nitrogen and for oxygen. As will be shown in a later paper, these groups are not only able to combine with nitrogen to form compounds of the ammonium type, but under suitable conditions they also combine with oxygen to form stable compounds of the oxonium type.

# Summary

The compounds of the alkyl tin and the alkyl mercury halides with ammonia and the amines have been investigated. It has been shown that trimethyl tin chloride and iodide combine with two molecules of ammonia, only one of which is firmly held. Trimethyl tin chloride combines with one molecule of aniline and pyridine, respectively. Trimethyl tin iodide combines with one molecule of pyridine. In the case of aniline, trimethyl tin iodide forms a compound containing two molecules of the former. Dimethyl tin chloride combines with two molecules of ammonia. Ethyl mercuric chloride and amyl mercuric iodide combine each with one molecule of ammonia.

It is pointed out that the results do not agree well with Werner's theory, as outlined by Werner and Pfeiffer. It is suggested that the properties of the resulting compounds are more rationally accounted for on the assumption that the alkyl metal group is transferred from the halogen atom to the nitrogen atom of the amine, thus forming a compound of the ammonium type.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

# THE ADDITION OF NITROGEN TRICHLORIDE TO UNSATURATED HYDROCARBONS. I

By G. H. Coleman and H. P. Howells Received September 11, 1923

In a recent study¹ of the chlorinating action of nitrogen trichloride on benzene and toluene, it was found that small amounts of chloro-amines were formed, presumably by the addition of nitrogen trichloride to the aromatic nucleus. The products obtained in each case proved to be mixtures of chlorinated amines which could not easily be separated.

The present investigation was undertaken to determine whether such an addition might not occur with hydrocarbons of the ethylene series with the formation of a single product. The hydrocarbons used were 2-butene, 1-butene, and trimethylethylene. The reactions were carried out in carbon tetrachloride solution, well cooled with a freezing mixture.

With 2-butene the reaction takes place fairly rapidly with the formation of a moderate yield of 2-chloro-3-dichloro-amino-butane, CH₃CHNCl₂-CHClCH₃, considerable free nitrogen, and a small amount of ammonium chloride. The above chloro-amine was not isolated as such, but by treatment with concd. hydrochloric acid was reduced to the corresponding 2-chloro-3-amino-butane, CH₃CHNH₂CHClCH₃. A possible explanation of this action of hydrochloric acid has been given by Coleman and Noyes.¹ A similar action of hydrogen chloride on a chloro-amine in ether solution is mentioned by Berg.²

With 1-butene the reaction occurs more slowly and a larger excess of the unsaturated hydrocarbon is required. The yield of amine is slightly less than with 2-butene. The amounts of free nitrogen and ammonium chloride are about the same. In this reaction there are, of course, two possible structures for the addition product, CH₃CH₂CHNCl₂CH₂Cl and CH₃CH₂-CHClCH₂NCl₂. On the basis of Markownikoff's rule³ for such addition reactions the position taken by the dichloro-amino group might have a bearing on the polarity of the chlorine in nitrogen trichloride. If it is assumed that the chlorine is positive, then according to this rule the dichloro-amino group should be attached to the second carbon atom from the end. This was shown to be the case by reduction of the product to 2-amino-butane. No evidence of the formation of the other possible isomer was obtained.

Racemic sec-butyl amine (2-amino-butane) has been prepared by

¹ Coleman and Noyes, This Journal, 43, 2213 (1921).

<sup>Berg, Chem. Zentr., [3] 7, 542 (1892).
Markownikoff, Ann., 153, 256 (1870).</sup> 

Pope and Gibson⁴ by the reduction of methylethyl ketoxime. In order to compare this compound with our product the work of these authors was repeated. The melting point of the benzoyl derivative was found to be several degrees higher than that recorded (see Experimental Part), but it agreed exactly with that of our product obtained through the reduction of the chloro-amine. A mixture of these substances melted at the same temperature. The *p*-nitrobenzoyl derivatives prepared by the two series of reactions were also found to be identical.

If in the addition of nitrogen trichloride to 1-butene the dichloro-amino group had added to the end carbon atom, then by reduction n-butylamine would be formed. The derivatives of n-butylamine do not correspond in physical properties to the same derivatives of the amine obtained in this investigation.

The reaction with trimethylethylene differs from those described above in that it is more rapid, a greater proportion of ammonium chloride is formed, and no amine is obtained from the reaction mixture. In fact, all but a trace of the nitrogen used can be accounted for as ammonium chloride and free nitrogen.

The formation of ammonium chloride in these reactions, and particularly in the last one where the proportion of this compound is considerably greater, is no doubt due to the reaction of nitrogen trichloride with hydrochloric acid, which may split out from the addition product first formed with the unsaturated hydrocarbon. Noyes⁵ has shown that nitrogen trichloride and hydrochloric acid yield ammonium chloride and chlorine quantitatively even in the absence of water.

The complete decomposition of the addition product which is probably first formed with trimethylethylene may be connected with the presence of a tertiary carbon atom in this compound and the fact that the nitrogen is very likely attached to this atom. Marvel⁶ has recently shown that in dialkyl mercury compounds the carbon-mercury linkage is much more easily broken when mercury is attached to a tertiary alkyl group than when it is attached to a secondary or a primary alkyl group. These facts are in agreement with what is already known concerning alcohols, halides and other compounds. By the action of chlorine on trimethylethylene Hell⁷ obtained monochloro-amylene,  $C_5H_9Cl_3$  amylene dichloride,  $C_5H_1oCl_2$ ; and chloro-amylene chloride,  $C_5H_9Cl_3$ . He concludes that a part of the amylene dichloride first formed must split out hydrochloric acid. The resulting unsaturated monochloro-amylene would then in part react with more chlorine. In the present work both the dichloro and the trichloro com-

⁴ Pope and Gibson, J. Chem. Soc., 101, 1702 (1912).

⁵ Noves. This Journal, 42, 2173 (1920).

Marvel, ibid., 45, 820 (1923).

⁷ Hell, Ber., 24, 217 (1891).

pounds were found, but the presence of monochloro-amylene was not definitely proved.

The investigation is being continued in this Laboratory with other unsaturated compounds and also with reference to a possible increase in the yields obtained.

# **Experimental Part**

#### The Reaction with 2-Butene

The preparation and analysis of nitrogen trichloride was carried out as described by Coleman and Noyes, with some slight modifications. Carbon tetrachloride was used as the solvent for the trichloride. The temperature of the cooling bath was maintained at 0– $10^{\circ}$ ; N ammonium nitrate solution was used as the source of the ammonia. After the addition of the chlorine the aqueous solution was removed and the carbon tetrachloride stirred for a short time with a little fresh ammonium nitrate solution. This was repeated a second time to insure the removal of any excess chlorine. Solutions containing as much as 20% of nitrogen trichloride were prepared but, in general, it was found best to use more dilute solutions.

The 2-butene was prepared from sec-butyl iodide and alcoholic potassium hydroxide, according to the method described by de Luynes.8 After it was washed and dried, the gas was passed into dry carbon tetrachloride, surrounded by a cooling bath. The reaction was carried out by adding the nitrogen trichloride solution through a dropping funnel, slowly, to the solution of the unsaturated compound contained in a flask surrounded by a freezing mixture of ice and salt (-10°). The apparatus was so arranged that the solution could be agitated during the addition, and any gas evolved could be collected and measured. When the yellow color of the nitrogen trichloride had completely disappeared, the solution was washed several times with water to remove any ammonium chloride. After it had been carefully separated from the water it was thoroughly shaken with 30-40 cc. of concd. hydrochloric acid. It was found desirable to have enough excess butene present to unite with the chlorine liberated at this point, in the reaction between the acid and the chloro-amine. If necessary, more of the butene solution was added. The hydrochloric acid was diluted with water and separated from the carbon tetrachloride. This acid solution now contained the hydrochloride of 2-chloro-3-amino-butane.

The reduction of the chloro-amine can also be effected by shaking it with an acid sulfite solution, but the reaction is not as complete as with concd. hydrochloric acid. It is interesting to note here that while these aliphatic chloro-amines can be quite easily reduced with an acid sulfite, the chloro-amines obtained by Coleman and Noyes¹ from benzene and toluene were reduced with difficulty, or not at all, by this reagent.

⁸ De Luynes, Ann., 132, 275 (1864).

The amounts used in a typical run were as follows.

One hundred and fifty-six mg. mols. of nitrogen trichloride in 400 g. of carbon tetrachloride; 220 mg. mols of 2-butene (determined by titration with bromine) in 400 g. of carbon tetrachloride. In this run there was formed 11 mg. mols. of ammonium chloride and 45.5 mg. mols. of the amine (isolated as the benzoyl derivative). The remainder of the nitrogen was given off as a gas during the reaction.

r-Benzoyl-2-chloro-3-amino-butane.—The benzoyl derivative of the amine was prepared from the solution of the hydrochloride above, by the usual Schotten-Baumann method; 9.6 g. was obtained, which is 29% calculated from the nitrogen trichloride. This was recrystallized several times from petroleum ether (b. p., 100–110°). Colorless needle-like crystals were formed, melting at 105–106° (uncorr.). The substance was analyzed for nitrogen by the Gunning-Arnold-Dyer modification of Kjeldahl's method, and for chlorine by the sodium peroxide bomb method described by Lemp and Broderson.

Analyses. Subs., 0.1526, 0.2237: 7.25, 10.8 ec. of 0.1 N HCl. Calc. for  $C_{11}H_{14}$ -ONCl: N, 6.63. Found: 6.65, 6.76.

Subs., 0.1726, 0.1523: 8.18, 7.21 cc. of 0.1 N AgNO₃. Calc. for  $C_{11}H_{14}ONCI$ : Cl, 16.80. Found: 16.83, 16.80.

### . The Reaction with 1-Butene

1-Butene was prepared from *n*-butyl iodide and alcoholic potassium hydroxide according to the method of Grabowsky and Saytzeff.¹⁰ The apparatus used and the method of carrying out the reaction were the same as given above, for 2-butene. In this case, however, a larger excess of the unsaturated compound was necessary, and a longer time was required for the color of the nitrogen trichloride to disappear. The carbon tetrachloride solution was shaken with water to remove ammonium chloride, then with concd. hydrochloric acid as before. The amounts used in a typical run were the following: 150 mg. mols. of nitrogen trichloride in 400 g. of carbon tetrachloride, 260 mg. mols. of 1-butene in 400 g. of carbon tetrachloride; 11.3 mg. mols. of ammonium chloride was formed, 35.5 mg. mols. of amine, and the remainder of the nitrogen was liberated as a gas.

r-Benzoyl-1-chloro-2-amino-butane.—One-third of the hydrochloric acid solution was used for the preparation of the benzoyl derivative by the Schotten-Baumann method;  $2.5 \, \mathrm{g}$ . of substance was obtained, which is a yield of 23.6%. The product was recrystallized several times from petroleum ether (b. p.,  $100-110^{\circ}$ ). Fine, silky needles in small clusters were formed, melting at  $91-92^{\circ}$  (uncorr.). Careful working up of the mother liquors failed to indicate the presence of more than one compound.

Analyses. Subs., 0.1520, 0.1744: 7.25, 8.36 cc. of 0.1 N HCl. Calc. for  $C_{11}H_{14}$ -ONCl: N, 6.63. Found: 6.68, 6.71.

Subs., 0.1670, 0.1504: 7.96, 7.15 cc. of 0.1 N AgNO₃. Calc. for  $C_{11}H_{14}ONCl$ : Cl, 16.80. Found: 16.90, 16.87.

r-Benzoyl-2-amino-butane.—The remaining two-thirds of the hydrochloric acid solution described above was cooled and nearly neutralized with sodium hydroxide. An excess of 2.5% sodium amalgam was then slowly added. The solution was stirred with a mechanical stirrer, and kept slightly acid to litmus by the addition of concd. hy-

Lemp and Broderson, This Journal, 39, 2069 (1917).

¹⁰ Grabowsky and Saytzeff, Ann., 179, 330 (1875).

drochloric acid as required. The amalgam was made by the modification of Nef's method, described by Raiford and Clark. After separating the solution from the mercury, one-half was used for the preparation of the benzoyl derivative; 1.5 g. was obtained, which after recrystallizing from petroleum ether (b. p., 100–110°), formed colorless needles, melting at 84–85° (uncorr.). The substance was found to contain no chlorine.

Analyses. Subs., 0.2302, 0.0945: 12.9, 5.36 cc. of 0.1 N HCl. Calc. for  $C_{11}H_{15}$ -ON: N, 7.92. Found: 7.84, 7.94.

In order to characterize the compound further the other half of the solution described above was used for the preparation of the p-nitrobenzoyl derivative. After recrystallizing several times from petroleum ether (b. p., 120–150°), the substance melted at 114.5–115.5° (uncorr.). As mentioned above, Pope and Gibson⁴ prepared racemic sec-butylamine (2-amino-butane) by the reduction of methylethyl ketoxime with sodium amalgam. The melting point of the benzoyl derivative recrystallized from aqueous alcohol is recorded as 75–76°. This compound was prepared as described by these authors and after recrystallizing several times from petroleum ether (b. p., 100–110°), melted at 84–85° (uncorr.). A mixture of this compound with r-benzoyl-2-amino-butane, obtained through the reduction of the chloro-amine, melted at the same temperature.

The p-nitrobenzoyl derivative was also prepared from the amine obtained by the reduction of the ketoxime. After recrystallizing from petroleum ether (b. p., 120–150°) this product melted at 114.5–115.5° (uncorr.). When mixed with r-(p-nitrobenzoyl)-2-amino-butane obtained through the reduction of the chloro-amine no change in melting point was observed.

p-Nitrobenzoyl-n-butylamine.—If, as stated above, in the addition of nitrogen trichloride to 1-butene the dichloro-amino group had added to the end carbon atom to form CH₃CH₂CHClCHNCl₂, then by reduction n-butylamine would be formed. The benzoyl derivative of n-butylamine was prepared. This was a clear oil, soluble in hot petroleum ether, and was not obtained in crystalline form. The p-nitrobenzoyl derivative was prepared, and after recrystallizing from petroleum ether (b. p., 120–150°) melted at 102.5–103° (uncorr.).

# The Reaction with Trimethylethylene

Nitrogen trichloride reacted very rapidly with trimethylethylene. During the addition of the trichloride solution, the yellow color disappeared very quickly as long as there was an excess of the unsaturated compound present, nitrogen gas was given off and a heavy white precipitate of ammonium chloride was formed. The ammonium chloride was filtered off, and the carbon tetrachloride tested for the presence of an amine. None was found. The white precipitate was washed with carbon tetrachloride and dried. Analysis for chlorine showed it to be ammonium chloride.

Analysis. Subs., 0.2102: AgCl, 0.5648. Calc. for NH₄Cl; Cl, 66.33. Found: 66.49.

The following table gives the amounts of the materials used and the products formed in three typical runs. The nitrogen trichloride was in each case dissolved in about 320 g. of carbon tetrachloride and the trimethylethylene in about 240 g. of carbon tetrachloride.

¹¹ Raiford and Clark, This Journal, 45, 1738 (1923).

Table I
Nitrogen Trichloride with Trimethylethylene

	I	II	III	
	,	—Mg. mols.——		
$C_5H_{10}$	100	100	100	
$NCl_3$	50.4	55.3	57.7	
NH ₄ Cl	14.5	15.5	16.1	
$N_2$ , mg. atoms	35.6	39.2	37.7	

Careful fractionation of the carbon tetrachloride solutions from the three runs yielded two very definite fractions with boiling points above that of carbon tetrachloride, one at 130–133° and the other at 174–180°. There was little or no indication of a fraction corresponding to monochloro-amylene. According to Hell⁷ monochloro-amylene,  $C_5H_9Cl_3$ , amylene dichloride,  $C_5H_10Cl_2$ , and chloro-amylene chloride,  $C_5H_9Cl_3$ , boil at 92–93°, 130–133°, and 174–180°, respectively.

Chlorine determinations were made by Carius' method on the two fractions mentioned.

Analyses. Fraction 130-133°. Subs., 0.1662: AgCl, 0.3335. Calc. for C₅H₁₀Cl₂: Cl, 50.35. Found: 49.93.

Fraction 174–180°. Subs., 0.2098: AgCl, 0.5127. Calc. for  $C_5H_9Cl_5$ : Cl, 60.45. Found: 60.66.

# Summary

- 1. Nitrogen trichloride adds to 2-butene to form 2-chloro-3-dichloro-amino-butane. This amine is reduced by concd. hydrochloric acid to 2-chloro-3-amino-butane.
- 2. Nitrogen trichloride adds to 1-butene to form 1-chloro-2-dichloro-amino-butane. The structure of this product was proved by reduction to 2-amino-butane (sec-butylamine).
- 3. According to Markownikoff's rule, the addition of nitrogen trichloride to 1-butene to form 1-chloro-2-dichloro-amino-butane, agrees with the assumption that the chlorine in nitrogen trichloride is positive.
- 4. Nitrogen trichloride reacts rapidly with trimethylethylene to form ammonium chloride, nitrogen, and amylene chlorides.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE UNIVERSITY OF NOTRE DAME]

# THE CATALYTIC CONDENSATION OF ACETYLENE WITH BENZENE AND ITS HOMOLOGS

By Joseph S. Reichert and J. A. Nieuwland Received September 20, 1923

# The Preparation of Diphenylethane

Unsymmetrical diphenylethane has been prepared¹ by the condensation of benzene with paraldehyde in the presence of concd. sulfuric acid. It has been demonstrated that acetylene may be substituted for acetaldehyde in the preparation of quinaldine² and the acetals.³ The method described in this paper consists in the similar substitution of acetylene for acetaldehyde in the preparation of diphenylethane from benzene and paraldehyde according to Baeyer. This synthesis may in a general way be represented by the equation,  $C_2H_2 + 2C_6H_6 \longrightarrow CH_3CH(C_6H_5)_2$ . Acetylene does not combine with benzene directly as indicated in this equation. However, when acetylene is passed into a mixture of benzene and concd. sulfuric acid in the presence of a mercury salt as a catalyst, the condensation of acetylene and benzene into diphenylethane is readily effected.

Experimental Part.—A mixture of 500 cc. of benzene, 50 cc. of concd. sulfuric acid and 5 g. of mercuric sulfate was put into a flask fitted with a 2-hole stopper, one hole of which was closed with a glass rod, the other fitted with a glass tube bent at a right angle. The flask was then tared and connected with a gasometer containing acetylene under a pressure of about 1.5 meters of water. The acetylene was washed through coned. sulfuric acid. The system was swept free from air by removing the glass rod from the stopper. The absorption of acetylene took place quite rapidly with the evolution of considerable heat. The flask was cooled by immersion in ice water. The absorption was continued until approximately three-fourths to four-fifths of the calculated amount of acetylene had been absorbed. During the absorption the reaction mixture turned first yellow and then brown. With the proper cooling there was little evidence of the formation of tarry or solid products. The absorption was completed in from two and one-half to three hours. To isolate the products, the reaction mixture was diluted with four times its volume of water and neutralized with sodium carbonate. The emulsion which formed upon the addition of sodium carbonate was broken by heat and the addition of common salt, or by extraction with ether. The two layers were then separated. and the upper layer which contained the hydrocarbons was subjected to a fractional distillation. Between 75° and 105° some unchanged benzene distilled. The temperature rose rapidly to 250° when diphenylethane commenced to distil. There was no evidence of decomposition until the temperature reached about 340°. By repeated fractionation diphenylethane was obtained; b. p., 268-272°. From the higher-boiling fraction a small amount of dimethylanthracene hydride was obtained. This product is formed by the condensation of two molecules of acetylene with two molecules of benzene. A yield of 40 to 50% of the calculated amount of diphenylethane referred to the amount of acetylene absorbed was obtained. The best yields were obtained when the reaction

¹ Baeyer, Ber., 7, 190 (1874).

² Nieuwland and Vogt, This Journal, 43, 2671 (1921).

³ Reichert, Bailey and Nieuwland, ibid., 45, 1552 (1923).

was allowed to take place at 10° to 20°. When the reaction took place without being cooled, the heat of reaction raised the temperature of the mixture up to 60° or 70°. Under these conditions the acetylene was absorbed even more rapidly but the yield of diphenylethane was thereby greatly reduced and instead of diphenylethane, products of a solid character were obtained. When the reaction was allowed to take place at higher temperatures there was evidence of the formation of sulfur dioxide also. It was thought possible that under the influence of the reduced mercury which is formed in small quantities in the reaction, the sulfuric acid might have oxidized the diphenylethane to benzophenone or the dimethylanthracene hydride to anthraquinone. These substances were, however, not found among the products of the reaction.

# The Preparation of the Homologs of Diphenylethane

Baeyer's method for the preparation of diphenylethane was applied by Fischer⁴ to the preparation of ditolylethane, namely, the condensation of toluene with paraldehyde in the presence of sulfuric acid. The process described in this paper consists in the substitution of acetylene for acetaldehyde in Fischer's method for the preparation of ditolylethane. Anschütz,⁵ who prepared diphenylethane and ditolylethane by the action of ethylidene chloride on benzene and toluene, respectively, likewise prepared dixylylethane by the same method. No reference was found in the literature to the preparation of dimesitylethane or ethylidene bis-ethylbenzene.

The method just described for the preparation of diphenylethane was found applicable to the preparation of its homologs. With toluene a 45 to 50% yield of ditolylethane (b. p., 295–300°), together with a small yield of tetramethylanthracene hydride was obtained. Xylene yielded 50 to 55% of dixylylethane (b. p., 322–326°) and a small amount of a high-boiling fraction, probably hexamethylanthracene hydride. Mesitylene, prepared by the condensation of acetone according to Bender and Erdmann, yielded 18 to 20% of dimesitylethane; b. p., 344–348°. The absence of a high-boiling fraction in this case coincides with the fact that the condensation of two molecules of acetylene with two molecules of mesitylene to form octamethylanthracene hydride is theoretically impossible. Ethyl benzene, prepared from ethyl bromide and bromobenzene according to Gattermann, yielded 20 to 25% of ethylidene bis-ethylbenzene, and a small amount of a high-boiling fraction, probably dimethyldiethylanthracene hydride. Both dimesitylethane and ethylidene bis-ethylbenzene are fluorescent and like their homologs boil without decomposition.

# Summary

A new and practical method for the preparation of diphenylethane, ditolylethane and dixylylethane is described. This method consists in the condensation of acetylene with benzene, toluene and xylene, respectively, in the presence of concd. sulfuric acid and a mercury salt.

This method has been applied to the preparation of the two compounds, dimesitylethane and ethylidene bis-ethylbenzene.

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⁴ Fischer, Ber., 7, 1193 (1874).

⁵ Anschütz, Ann., 235, 326 (1886).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TUFTS COLLEGE]

# THE ACTION OF HYDROXYLAMINE AND OF HYDRAZINE ON THE ARYL MONOTHIO AMIDES OF CARBETHOXY-ETHYLMALONATE

By DAVID E. WORRALL

RECEIVED SEPTEMBER 29, 1923

The addition products obtained by the action of phenyl mustard oil and para substituted mustard oils on ethyl aceto-acetate were shown in a previous communication¹ to be useful for the preparation of heterocyclic compounds of the isoxazole and pyrazole series. The reagents used were hydroxylamine and hydrazine. Similar series of reactions have been found to take place with the corresponding mustard oil addition products of malonic ester.

Thus, carbethoxy-ethylmalonate monothio-anilide, formed by the action of phenyl mustard oil on diethylmalonate reacts with hydroxylamine as follows:  $CS(NHC_6H_5)CH(COOC_2H_5)COOC_2H_5 + NH_2OH = H_2S + C(NHC_6H_5)CH(COOC_2H_5)CO + C_2H_5OH$ .

The actual product obtained is the hydroxylamine salt of the above compound; consequently, it is necessary to use two equivalents of the base. The free isoxazole is obtained by decomposition of the salt with hydrochloric acid. It is less basic than the corresponding isoxazole obtained from aceto-acetic ester and does not form a salt with acids. It is insoluble even in warm coned. hydrochloric acid. It readily dissolves in dil. sodium hydroxide solution, changing to a sodium salt.

Hydrazine reacts with carbethoxy-ethylmalonate monothio-anilide to form a pyrazole:  $CS(NHC_6H_5)CH(COOC_2H_5)COOC_2H_5 + NH_2NH_2 = H_2S + C(NHC_6H_5)CH(COOC_2H_5)CO + C_2H_5OH.$ 

N-----NH

The pyrazole is soluble in warm concd. hydrochloric acid solution and is also soluble in sodium hydroxide solution from which the sodium salt may be isolated.

The series of reactions starting with malonic ester and resulting ultimately in isoxazoles and pyrazoles is somewhat less restricted in scope than the series beginning with ethyl aceto-acetate. This is due to the fact that the addition products of *ortho* and *meta* substituted mustard oils to ethyl aceto-acetate undergo hydrolysis so readily to the thio amides of acetic acid that ring formation is not possible.\(^1\) No such difficulty presents itself in the malonic ester series.

¹ Worrall, This Journal, 44, 1551 (1922).

# Experimental Part

carbethoxy-ethylmalonate monothio-anilide were added 2 equivalents of free hydroxylamine dissolved in approximately 80 cc. of alcohol and prepared by neutralization of the hydrochloride with potassium hydrogen carbonate. The mixture was heated under a reflux condenser for 6 hours and then poured into a beaker where it rapidly solidified to a sticky cake. This product was dried on a porous plate, stirred with 50 cc. of warm water with which it formed a thick paste, and 10 cc. of dil. hydrochloric acid was added. A gum formed as a result of the action of the acid, but it quickly changed to a compact crystalline substance, easy to manipulate; yield, 6.5 g. Finally, the isoxazole was further purified by two crystallizations from an alcohol.

Analyses. Calc. for C₁₂H₁₂O₄N₂: C, 58.1; H, 4.8. Found: C, 58.4; H, 4.6.

It is readily soluble in hot alcohol from which it separates in small, stout needles softening at 160° and melting at 166° with foaming, due to the evolution of carbon dioxide, accompanied by decomposition.

Permanganate solution is decolorized in the cold by the isoxazole, resulting in the formation of phenyl isonitrile. It reacts with bromine in glacial acetic acid solution to form a crystalline derivative, but it is changed to a tar by concd. nitric acid. It is insoluble in concd. hydrochloric acid even when warmed and sparingly soluble in hot water. Warm sodium hydroxide solution easily dissolves the substance, forming a sodium salt that separates in the form of slender needles as the solution cools. A mustard-colored copper salt is precipitated from hot water solution by copper acetate.

3-Anilino-4-carbethoxy-5-oxy-pyrazole, COOC₂H₅.HC—CNHC₆H₅.—Two equiv-



alents of free hydrazine, prepared from the sulfate by neutralization with potassium hydrogen carbonate, dissolved in 80 cc. of alcohol were added to 10 g. of carbethoxyethylmalonate monothio-anilide. The mixture was heated under a reflux condenser for 4 to 5 hours. A dark green color developed at first but subsequently disappeared. The bulky crystalline product that formed on standing was filtered with suction, washed with a few cubic centimeters of cold water and mixed with approximately 50 cc. of water containing 10 cc. of dil. hydrochloric acid. No apparent change took place. The product was filtered by suction and recrystallized from 100 cc. of alcohol; yield, approximately 5 g.

Analyses. Calc. for C12H13O3N3: C, 58.3; H, 5.3. Found: C, 58.2; H, 5.2.

The pyrazole is sparingly soluble in hot water and somewhat more soluble in hot alcohol. A voluminous precipitate of fluffy white needles separated as the solution cooled. It softened at 187°, partially melting with decomposition at 194–195°. It decolorized both permanganate solution and bromine dissolved in carbon tetrachloride, and was violently acted upon by concd. nitric acid to form a black tar. A sodium salt, lustrous white leaves rapidly hydrolyzed by hot water, formed when the material was warmed with sodium hydroxide solution.

3-o-Toluidino-4-carbethoxy-5-isoxazole, COOC₂H₅.C₃H₂ON.NHC₆H₄CH₃.—A mixture of 10 g. of crude² carbethoxy-ethylmalonate monothio-o-toluide with two equivalents of hydroxylamine in alcohol solution was heated for 6 hours under a reflux condensity.

² The thio compound obtained by the action of o-tolyl mustard oil on malonic ester did not crystallize on standing; hence it had to be used without purification.

ser. The product which separated on cooling was filtered with suction, decomposed with hydrochloric acid and twice crystallized from alcohol; yield of purified substance, approximately 2 g.

Analyses. Calc. for C12H14O4N2: C, 59.5; H, 5.3. Found: C, 59.2; H, 5.1. -

The isoxazole crystallizes from alcohol in flat needles and plates melting with decomposition at  $165-167^{\circ}$  with preliminary softening.

3-o-Toluidino-4-carbethoxy-5-oxy-pyrazole, COOC₂H₅.C₂H₂ON₂.NHC₆H₄CH₃.—A mixture of 10 g. of crude carbethoxy-ethylmalonate monothio-o-toluide with an alcoholic solution of two equivalents of hydrazine was heated until no further evolution of hydrogen sulfide took place. The precipitate which formed on cooling was treated with hydrochloric acid to free it from hydroxylamine, filtered off and twice crystallized from alcohol; yield, approximately 2 g.

Analyses. Calc. for  $C_{13}H_{15}O_{2}N_{3}$ : C, 59.8; H, 5.7. Found: C, 59.4; H, 5.5.

The pyrazole separates from alcohol in flocks of feathery, white needles. It softens at 205°, partially melting with decomposition at 215°.

3-p-Toluidino-4-carbethoxy-5-oxy-isoxazole,  $COOC_2H_5$ . $C_3H_2O_2N$ .CHNC $_6H_4CH_3$ .—A mixture of 10 g, of carbethoxy-ethylmalonate monothio-p-toluide with two equivalents of hydroxylamine in alcoholic solution was heated under a reflux condenser for 5 hours. Then 4 cc. of concd. hydrochloric acid was added directly to the hot alcoholic solution. Since the resulting precipitate contained considerable inorganic material it was twice digested with 25 cc. of warm water, cooled and filtered with suction; yield, 5.2 g. The product was finally crystallized from alcohol.

Analyses. Calc. for C₁₃H₁₄O₄N₂: C, 59.5; H, 5.3. Found: 59.7; H, 5.3.

The p-toluidino-isoxazole separates from alcohol in needles and plates melting with decomposition at 172–173°.

3-p-Toluidino-4-carbethoxy-5-oxy-pyrazole, COOC₂H₅.C₃H₂ON₂.NHC₆H₄CH₅.—A mixture of 10 g. of carbethoxy-ethylmalonate monothio-p-toluide with two equivalents of hydrazine in alcoholic solution was heated under a reflux condenser for four hours; 5 cc. of concd. hydrochloric acid was added to the mixture while it was still warm. The product was thoroughly washed with water and then was crystallized from alcohol; yield of purified substance, 4 g.

Analyses. Calc. for C13H15O3N3: C, 59.8; H, 5.7. Found: C, 60.0; H, 5.7.

The pyrazole separates from alcohol as a bulky precipitate of feathery needles. When heated above 200° it undergoes slow decomposition without melting.

3-p-Bromo-anilino-4-carbethoxy-5-oxy-isoxazole, COOC₂H₅.C₃HO₂N.NHC₆H₄Br.— Five g. of carbethoxy-ethylmalonate monothio-p-bromo-anilide was treated in the customary manner with hydroxylamine, the product decomposed with acid and purified by crystallization from alcohol; yield of purified compound, 2.4 g.

Analysis. Calc. for C₁₂H₁₁O₄N₂Br: Br, 24.5. Found: 24.1.

The bromo-anilino-isoxazole separates from alcohol in slender needles which slowly sinter together and melt with decomposition at 163-170°.

3-p-Bromo-anilino-4-carbethoxy-5-oxy-pyrazole,  $COOC_2H_5$ . $C_3H_2ON_2$ . $NHC_6H_4Br$ .— Five g. of carbethoxy-ethylmalonate monothio-p-bromo-anilide was heated in alcohol solution with two equivalents of hydrazine, the product treated with acid and recrystallized from alcohol.

Analysis. Calc. for C12H12O3N3Br: Br, 24.5. Found: 24.2.

The new pyrazole separates from alcohol in small fluffy needles, which soften at  $212\,^\circ$  and melted at  $217\,^\circ$ .

# Summary

The addition products obtained by the action of phenyl, o-tolyl and p-bromo mustard oils on diethylmalonate condense with hydroxylamine and hydrazine to form, respectively, isoxazoles and pyrazoles.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# THE KETENIC DECOMPOSITION OF KETONES. KETENE AND METHYL KETENE

By Charles DeWitt Hurd Received October 3, 1923

Undoubtedly, the best way to prepare ketene is to decompose acetone vapors at high temperatures. Recently, it has been demonstrated that ketene may be prepared in a similar manner, but with poorer yields, from methylethyl ketone. It was considered probable that methyl ketene would also be formed in this reaction, but there seemed to be no positive evidence for such an occurrence.¹

Ketene was identified as acetanilide, its reaction product with aniline. Methyl ketene would have formed propionanilide. This was not isolated, but there was found an unidentified crystalline product that melted at 80°, about 25° lower than the melting point of propionanilide. A similar low-melting toluidine reaction product was observed. One purpose of the present investigation was to establish the identity of these substances.

A second problem with which this paper deals was to ascertain whether or not methyl ketene was decomposed by heat. An opinion was expressed by Hurd and Kocour² that methyl ketene may actually have been prepared in their experiment, but that it may have decomposed at the temperature to which it was exposed. In order to answer this question, it was approached from two angles. First, an apparatus was built which heated the ketone vapors for a briefer period of time than formerly. The heating unit of this consisted of an electrically heated platinum filament, described below. If methyl ketene is susceptible to heat, an apparatus of this type should result in an augmented yield of methyl ketene. It seems probable that a short combustion furnace instead of the long one employed formerly, might also produce an increased yield of methyl ketene. This idea has not been tried experimentally as yet, however.

In the second place, a study was made of the ketenic decomposition of diethyl ketone. Because of its symmetrical structure, this ketone should

¹ (a) Hurd and Kocour, This Journal, 45, 2167 (1923). For the preparation of ketene from acetone, see (b) Hurd and Cochran, *ibid.*, 45, 515 (1923); also, a footnote to the article by Hurd and Kocour.

² Ref. la, p. 2168.

give as a primary decomposition product, methyl ketene:  $CH_3$ — $CH_2$ —CO— $C_2H_5$   $\longrightarrow$   $CH_3$ —CH=CO +  $C_2H_6$ . There is no chance for other ketenes to be formed, except as decomposition products of the methyl ketene. Therefore, it bears upon the question to study this reaction and to study the fate of the methyl ketene.

The general results may be conveniently classified under three headings: (1) comparison of results due to the change of apparatus; (2) the identity of the low-melting aniline (or toluidine) reaction product, noted in the paper of Hurd and Kocour; and (3) the behavior of diethyl ketone towards heat.

1. Acetone vapors give a better yield of ketene with the former apparatus, namely, the long combustion furnace. Methylethyl ketone, on the contrary, gave with the present platinum wire apparatus both a better yield of ketene, identified as acetanilide, and also a larger quantity of the 80° material. No work was done with diethyl ketone in the former type of apparatus. This substance was decomposed by the hot platinum wire filament, however, to produce both ketene and methyl ketene in comparatively high yields. This is discussed in more detail below.

Diethyl ketone formed a considerable quantity of higher-boiling condensation products, and very little of the original ketone could be recovered in the distillate. In this respect, it differed from acetone and methylethyl ketone. With diethyl ketone, also, a larger carbon deposit was formed in the apparatus.

- 2. The 80° material was shown to be a mixture of acetanilide and propionanilide. This was indicated by its appearance and by its solubility characteristics. It was conclusively demonstrated by tests and by analysis. A mixture with identical properties was prepared from pure acetanilide and pure propionanilide. To form it, merely recrystallization of these 2 anilides from appropriate solvents was necessary. Similarly, the low-melting substance formed when toluidine was used in the place of aniline was found to be a mixture of aceto- and propiono-toluidides. Both of these mixtures appeared homogeneous, both melted completely within 0.5°, and both solidified rapidly when cooled a few degrees below the melting point. Several recrystallizations from various solvents did not change the melting point. Therefore, it was erroneously thought for a time that the substances might be pure chemical individuals. That they are mixtures, however, is now settled definitely.
- 3. It will be recalled that methyl ketene alone was anticipated in the decomposition of diethyl ketone. However, both ketene and methyl ketene were shown to be present. It appears rather obvious that ketene could not have been a primary decomposition product of diethyl ketone. Preferably, ketene must have been formed by the action of heat upon methyl ketene, which is a primary decomposition product. This would

indicate that the methyl ketene molecule will rupture at the single bond, CH₃—CHCO, to form ketene and ethylene. Undoubtedly, the molecule also is ruptured at the double bond, CH₃CH—CO, to form butylene, or its decomposition products, and carbon monoxide. Both of these decompositions necessarily diminish the yield of methyl ketene.

The explanation that ketene is formed from methyl ketene is substantiated by a comparison of the relative yields of ketene and methyl ketene from the 2 ketones, methylethyl ketone and diethyl ketone. With methylethyl ketone, both acetanilide and propionanilide were formed as reaction products of the ketenes, but propionanilide could not be isolated as such. Diethyl ketone, however, must have given rise to a greater relative ratio of methyl ketene to ketene, because in this case it was possible to isolate propionanilide in the pure state by fractional recrystallization. The relatively lower yield of ketene from diethyl ketone is to be expected because it is formed only as a result of a secondary reaction, whereas two effects conspire to diminish the yield of methyl ketene from methylethyl ketone. The first is the fact that both ketene and methyl ketene are formed concurrently, and the second is that methyl ketene, once formed, is decomposed by heat. As was explained above, the relative yield of ketene is somewhat enriched by this decomposition.

Methyl ketene has been prepared previously by the action of zinc shavings upon  $\alpha$ -bromopropionyl bromide.³ The yield was small. Therefore, the present method is interesting since it is the only other method available by which methyl ketene may be obtained. It possesses the disadvantages that methyl ketene alone is not produced. However, it is anticipated that modifications of the experimental procedure may be found to eliminate the secondary reaction by which ketene is formed.

# Experimental Part

### Purification of the Three Ketones

The acetone was distilled, refluxed with a small quantity of potassium permanganate, and redistilled. The methylethyl ketone was the commercial product, purified by several fractional distillations, and was the same material as that used by Hurd and Kocour. The diethyl ketone was obtained from manufacturers who claimed for it the highest purity. The claim was an optimistic exaggeration; nevertheless, by fractionation, a good portion was obtained which distilled between 102° and 103.5°.

# Apparatus

The apparatus was built in 4 units, the first of which was the decomposition bulb. This, except for minor details, was similar to the apparatus used by Ott and Schmidt⁴ for the preparation of carbon suboxide from diacetyltartaric anhydride. It was blown from

³ Staudinger, Ber., 44, 535 (1911).

⁴ Ott and Schmidt, Ber., 55B, 2126 (1922).

76mm. Pyrex tubing. Such differences in detail as were adopted are as follows. The openings of the 2 glass tubes through which the copper wires entered the apparatus were made gas tight in the following manner. A copper wire was fused to each end of a solid brass rod, 2 cm. long and of the same diameter as the glass tube. One of the wires entered the glass tube and was pulled snugly so that the brass rod touched the glass. This permitted an air-tight seal to be made simply by covering the glass and brass with a piece of rubber tubing. The loose end of this copper wire was sealed to an end of the platinum wire filament. The copper wire, fastened to the other end of the brass rod, was connected with the electric current. The other opening was sealed in identical fashion.

The platinum wire filament was 0.3 mm. in diameter and about 165 cm. in length. The top of the glass support upon which this wire was mounted terminated with a glass handle to which the copper wires were fastened. Instead of employing an annular rubber washer between the ground glass joint of the upper and lower halves of the apparatus, the seal was effected by stopcock grease. Rubber would be essential if a constant high vacuum were to be maintained. That was not essential, nor was it desired in this experiment.

The second unit of the apparatus was a *condensing flask* for the distillate. This was a double-necked, round-bottomed flask, identical with the second unit of Ott's apparatus.⁴

The reaction tube formed the third unit. This consisted of a large U-tube, one arm of which was larger than the other. The small arm was connected to the second unit. The tube was of such capacity that 50 cc. of liquid filled the bottom and extended a short distance up the sides.

The fourth unit was a manometer and a vacuum oil pump. The vacuum was desirable in the apparatus to remove oxygen, to make any possible leaks inward ones, and to maintain a constant, rapid gaseous flow.

# Details of Manipulation and General Remarks

Previous to a run, there were placed in the decomposition bulb the desired amount of ketone, and in the reaction tube an excess of aniline (or toluidine) dissolved in xylene. The 4 units were then assembled and the condensing flask was surrounded by crushed ice. After the evacuation of the whole apparatus to about 20 mm., the electric current was turned on, and the resistance adjusted so that a current of 6 amperes was maintained. An asbestos board was inserted between the first two units. The pressure in the apparatus gradually rose to 300–400 mm. as the reaction progressed. This gain in pressure was characteristic of every run. It prevented a too rapid volatilization of the ketone. The duration of the runs, when a 50cc. sample of ketone was used, was about 2 hours. It was necessary in some cases to apply heat beneath the decomposition bulb to volatilize the final portion of ketone.

The first experiments were conducted in an atmosphere of carbon dioxide, but inasmuch as the results did not differ from those obtained when the original atmosphere before evacuation was air, this procedure was disregarded.

⁵ The copper-to-brass, and the copper-to-platinum joints are readily made with the flame of the blast lamp. The oxidized copper surface is reduced, while hot, by thrusting it into methanol.

⁶ When 2 tubes were used, the second was considerably smaller than the first.

# Decomposition of Acetone

Fifty cc. of acetone was vaporized and heated in the decomposition bulb during the course of 2 hours. The resistance wire was heated by a current of 6 amperes; 28 g. of aniline was used in 2 reaction tubes, 24 g. in the first, and 4 g. in the second. The aniline was diluted with xylene, about 28 cc. being used in the first tube and 6 cc. in the second. It was found that no more than traces of ketene escaped reaction in the first tube.

Nine cc. of distillate was collected in the condenser. For the most part, this was undecomposed acetone.

The xylene and the excess of aniline were removed by distillation. The acetanilide that remained was cooled and crystallized from a mixture of benzene and ligroin; m. p.,  $113-114^{\circ}$ ; yield,  $7.5 \, \mathrm{g}$ , or 9.8%, based upon the acetone that was not recovered.

There was some carbonization in the decomposition bulb.

### Decomposition of Methylethyl Ketone

Reaction with Aniline.—Fifty g. of methylethyl ketone was poured into the first bulb. Somewhat over 21 g. of freshly distilled aniline, diluted with 50 cc. of xylene was inserted in the reaction tube. Only a negligible amount of product was formed in a second reaction tube, placed in series with the first. The current used was 6 amperes; the duration of the experiment was 110 minutes.

Thirteen g. of distillate was collected, 14 cc. of which distilled between 76° and 83°. One cc. of foully smelling liquid remained. This did not solidify at —10°, nor was a solid obtained when part of it was evaporated. A solid was expected because crystals were noticed in the receiving arm of the condensing flask, early in the run; later, these dissolved in some of the liquid distillate. The same occurrence was noted in the decomposition of acetone.

The xylene was evaporated from the reaction product, following which the excess of aniline was removed by steam distillation. A non-volatile oil remained that solidified when the flask was cooled. This solid was filtered out and dissolved in hot alcohol. The aniline evidently had been imperfectly removed, for the addition of an equal volume of water caused the separation of oily crystals. These were collected and discarded; any possible reaction product contained therein was not calculated in the final yield. The filtrate was evaporated upon a watch glass nearly to dryness, and the crystals were collected upon a filter; weight, 2.6 g. The solid was insoluble in cold ligroin, only moderately soluble in cold carbon tetrachloride or in boiling ligroin (110°), and soluble in ethyl acetate. It was divided into 2 fractions by successive recrystallizations from these solvents or from appropriate mixtures of them. The more insoluble fraction was acetanilide; it melted at 110–112°. No purer product could be obtained by further crystallization.

By repeated recrystallizations of the more soluble portion, a fraction was obtained that melted sharply at 79.5–80°. The crystals were needle-shaped, and appeared to be perfectly homogeneous. In spite of the sharp melting point and the apparent homogeneity this material was proved to be not a chemical individual, but a mixture of acetanilide and propionanilide.

Analyses. Subs., 0.1368: CO₂, 0.3578; H₂O, 0.0892. Subs., 0.1551: N, 14.5 cc. (33.9°, 738.6 mm. (30.5°)), 40% KOH used. Calc. for  $C_6H_6N$ —COCH₃: C, 71.1; H, 6.71; N, 10.4. Calc. for  $C_6H_6N$ —COC₂H₅: C, 72.5; H, 7.45; N, 9.40. Found: C, 71.4; H, 7.28; N, 9.8.

An empirical formula, calculated from the observed values, is  $C_{\mathfrak{d} \cdot \mathfrak{d}}H_{\mathfrak{d} \cdot \mathfrak{d}}ON$ . This is seen to be between the two formulas,  $C_{\mathfrak{d}}H_{\mathfrak{d}}ON$  and  $C_{\mathfrak{d}}H_{\mathfrak{d} \cdot \mathfrak{d}}ON$ , required for acetanilide and propionanilide. In the above reaction, these two anilides must have been prepared from the reactions of ketene and methyl ketene with aniline. Further analytical proof

that the gaseous mixture of ketene and methyl ketene was formed is given below in the case of the toluidides.

To secure more evidence to confirm the belief that the 80° material was a mixture, an attempt was made to prepare such a mixture from the pure reagents. Slightly more acetanilide, m. p., 114°, than propionanilide, m. p., 103–104° (see p. 3101), was dissolved in a mixture of carbon tetrachloride and ligroin. The crystals that formed when the mixture was cooled were collected by filtration, and disregarded; m. p., 85–90°. The filtrate, however, was evaporated and the residue crystallized from boiling ligroin. Needle-shaped crystals resulted that melted sharply at 79–80°. These were identical in appearance with those formed in the work with methylethyl ketone. A mixed-melting-point determination of these two sets of 80° crystals gave 79–79.5°.

The 2.6 g. of reaction product corresponds to a yield of 3.7% if the material is assumed to be entirely acetanilide, or 3.4% if it is assumed to be propionanilide. This percentage is somewhat smaller than the true yield, for some of the reaction product was discarded, as explained above.

Reaction with p-Toluidine.—The details of this run were the same as those of the previous one, save that the aniline was replaced by 25 g. of p-toluidine. The p-toluidine had been previously recrystallized from benzene and ligroin. About 29.5 g. of methylethyl ketone entered the reaction; this was shown by the fact that there was 20.5 g. of distillate.

The xylene and the excess of toluidine were removed from the reaction product by vacuum distillation. The residue solidified quickly when cooled. It was crystallized from a mixture of benzene and ligroin. This material, which was later shown to be a mixture of acetotoluidide and propionotoluidide, weighed 3.2 g. Based upon the unrecovered ketone, this corresponds to a 5.3% yield of acetotoluidide, or a 4.8% yield of propionotoluidide.

The mixture was separated into two fractions both by crystallization from a mixture of carbon tetrachloride and ligroin, and by the use of each of these solvents independently. The more insoluble portion was acetotoluidide; m. p., 144°. The more soluble portion, m. p., 105.5–106°, was shown to be a mixture of acetotoluidide and propionotoluidide. The weight of the former was about 3.6 times that of the latter. Therefore, in this reaction, the ratio of methyl ketene to ketene is small.

Analyses (105.5–106° material). Subs., 0.1438:  $CO_2$ , 0.3846;  $H_2O$ , 0.0997. Subs., 0.1629: N, 13.4 cc. (32.5°, 744.3 mm. (31°)), 40% KOH used. Calc. for  $C_7H_8N$ —COCH₃: C, 72.5; H, 7.45; N, 9.40. Calc. for  $C_7H_8N$ —COC₂H₅: C, 73.6; H, 7.98; N, 8.60. Found: C, 73.0; H, 7.75; N, 8.73.

An empirical formula calculated from the experimental values is  $C_{9.8}H_{12.4}ON$ . Acetotoluidide is  $C_9H_{11}ON$  and propionotoluidide is  $C_{10}H_{12}ON$ .

# Decomposition of Diethyl Ketone

Forty g. of diethyl ketone and 14 g. of freshly distilled aniline were placed in the apparatus. The aniline was diluted with 50 cc. of xylene. Six amperes of current was used, and the duration of the experiment was 100 minutes. There was more carbonization on the surface of the decomposition bulb in this experiment than was the case with acetone or with methylethyl ketone, and very little recoverable ketone was found in the distillate. Instead, higher-boiling condensation products were formed. The 13 g. of liquid thus obtained distilled as follows: 2 g. between 100° and 110°; 2 g. between 110° and 124°; 7 g. between 124° and 150°; and 2 g. of higher-boiling residue. Thus, little

⁷ Various reactions of diethyl ketone are discussed by Samec, Monatsh., 28, 739 (1907).

of the ketone which did not decompose into gaseous products escaped decomposition. Twenty-seven g. may have undergone ketenic decomposition.

The xylene and the aniline were removed from the reaction product by vacuum distillation. The residue, which solidified as it cooled, was dissolved in hot carbon tetrachloride and was precipitated by ligroin; weight, 4.8 g. This corresponds to a yield of 10.3% assuming that the material is propionanilide, or 11.3%, assuming that the material is acetanilide. These yields are based upon 27 g. of diethyl ketone. It may be fairer to base the yield upon 40 g., since very little of the ketone was recovered as such. In this case the yields become 7.0% or 7.6%, respectively.

Both propionanilide, m. p., 101.5–102.5°, and acetanilide, m. p., 110–112°, were isolated from the reaction product. The solvents used were carbon tetrachloride and ligroin. Lower-melting mixtures of these two compounds were also obtained in the fractionation.

Propionanilide was prepared for purposes of comparison by refluxing 5 g. of aniline and 8 g. of propionic acid for 5 hours. A white solid was obtained when this liquid mass was poured into 100 cc. of cold water; weight, 6.5 g. A further yield of 0.7 g. was obtained by evaporation of the water. The solid, after recrystallization from a mixture of carbon tetrachloride and ligroin, melted at 103–104°. A mixture of this with equal parts of the 101.5–102.5° material melted at 102–103.5°.

No idea of the relative amounts of acetanilide and propionanilide was obtained. At least, there was enough propionanilide to be easily isolated, but it seemed that there was a greater quantity of acetanilide in the mixture.

### Summary

A further study of the ketenic decomposition of acetone and of methyl ketone has been made. Diethyl ketone, which has not been investigated heretofore in this connection, also was found to decompose ketenically. All three ketones give ketene as a decomposition product. Both methylethyl ketone and diethyl ketone produce methyl ketene, the larger relative yield coming from the latter.

A heating unit is described that differs from the apparatus used in the earlier work. It gives better results with methylethyl ketone and with diethyl ketone; with acetone, however, this is not the case.

Heat apparently ruptures the molecule of methyl ketone at the single bond to give ketene. This conclusion is reached because both ketene and methyl ketene were observed as decomposition products of diethyl ketone, whereas methyl ketene alone is accountable for as a primary decomposition product. The greater yield of methyl ketene when the ketone vapors were heated for a short period of time, in preference to a longer period, is further confirmation of the destructive effect of high temperatures upon methyl ketene. Decomposition undoubtedly occurs at the double bond as well as at the single bond, not to give another ketene as decomposition product, however.

Methyl ketene has been prepared by only one other method. Therefore, the present procedure, in spite of certain drawbacks, should prove to be of value.

URBANA, ILLINOIS

[Contribution from the Chemical Laboratory of the University of Illinois]

## ARSONO-ARYLAMINO ALCOHOLS

By C. W. Rodewald with Roger Adams¹ Received October 3, 1923

During the past few years many new organic arsenic compounds have been made in this Laboratory which have various types of substituted, nitrogen-containing groups in aryl arsonic acids. These have been prepared in order to determine whether the presence of the new groups might not cause a decrease in the toxicity of the products as compared with the corresponding arsanilic acids which may be looked upon as the basic substances of all these derivatives. This communication is a report on a part of this work involving the preparation of certain aryl arsonic acids containing  $\beta$ -hydroxyethylamino and  $\gamma$ -hydroxypropylamino groups. Arsenic compounds containing these groups are of special interest because these groups are found so frequently in naturally occurring and synthetic compounds of marked physiological action.

The procedure for their preparation is similar to that described for other  $\beta$ -arylamino-ethanols and  $\gamma$ -arylamino-propanols described recently by Adams and Segur, and Pierce and Adams. The amino-arylarsonic acids are dissolved in aqueous alkali and treated with  $\beta$ -chloro-ethyl chloroformate, yielding  $\beta$ -chloro-ethyl-(arsono-aryl) carbamates. These latter compounds when refluxed with 2 molecular equivalents of aqueous or alcoholic alkali yield arsono-aryl oxazolidones or when refluxed with excess of aqueous alkali yield the hydrolytic products of the arsono-aryl oxazolidones, namely,  $\beta$ -arsono-aryl amino-ethanols:  $H_2O_3AsC_6H_4NH_2 \longrightarrow H_2O_3AsC_6H_4NHCOOCH_2CH_2 \longrightarrow H_2O_3AsC_6H_4N-OOCH_2CH_2 \longrightarrow H_2O$ 

### HCH2CH2OH.

¹ This communication is an abstract of a portion of a thesis submitted by C. W. Rodewald in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Johnson and Adams, This Journal, 45, 1307 (1923). Quick and Adams, *ibid.*, 44, 805 (1922). Completed but as yet unpublished work at the University of Illinois comprises the formation of three new types of organic arsenic compounds.

³ Adams and Segur, ibid., 45, 785 (1923).

⁴ Pierce and Adams, ibid., 45, 790 (1923).

Analyreac

Various carbamates, oxazolidones or oxazones and  $\beta$ -amino-ethanols or  $\gamma$ -aminopropanols from different o- and p-amino-aryl-arsonic acids were prepared. All of the substances proved to be white crystalline compounds readily made and purified. Every one of these derivatives was less toxic than the corresponding arsanilic acid, but the amino alcohols were the least toxic of the different types of compounds. Moreover, the amino-alcohols were much less toxic than the arsanilic acids from which they were derived, the  $\beta$ -amino-ethanols being slightly less toxic than the corresponding  $\gamma$ -amino-propanols. The toxicities of these compounds were kindly tested by Dr. G. W. Raiziss of the Dermatological Laboratories of Philadelphia.

# Experimental Part

All of the compounds made in this investigation did not have distinct melting points owing to the decomposition which took place at the same time. The figures given, therefore, are those obtained as an average of a number of determinations. By varying the speed of heating the points are varied, sometimes as much as 10°.

 $\beta$ -Chloro-ethyl-(arsono-aryl) Carbamates.—To a solution of 1 molecular equivalent of amino-aryl-arsonic acid in about 8 times its weight of water and one equivalent of sodium hydroxide in 5 N solution was added in small portions with vigorous shaking or mechanical stirring, one molecular equivalent of  $\beta$ -chloro-ethyl chloroformate. Heat was developed during the reaction that took place and the temperature was kept below 35° by immersion of the flask from time to time in an ice-bath. The product separated as a granular precipitate during the course of the reaction. Shaking or stirring was continued for 10 minutes after the addition of the chloroformate in order to make certain of the completion of the reaction. Concd. hydrochloric acid was added in sufficient quantity to dissolve any small amount of unchanged amino-aryl-arsonic acid and the product was then filtered off and washed with water. The substances thus produced were very readily purified by crystallization from 30% acetic acid, forming in every case white needles. The carbamates were soluble in aqueous sodium carbonate or sodium bicarbonate.

# TABLE I CARBAMATES

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Substance		Yield	М. р. °С.	Wt. G.	Cc. of $0.0963~N$	Calc. I ₂ %	Found %
8-chloro-ethyl-(p-arsonophenyl)-	C9H11O5NClAs	93	> 250	0.3630	22.83	23.18	22.83
8-chloro-ethyl-(o-arsonophenyl)-		81	156-157	. 3630	23.02	23.18	23.02
8-chloro-ethyl-(2-methyl-5-arson-							
ophenyl)-	C10H13O5NClAs	68	193-195				
γ-chloropropyl-(p-arsonophenyl)-	C10H13O5NClAs	92	245-246	. 2047	12.65	22.26	22.43
γ-chloropropyl-(o-arsonophenyl)-	C10H13O5NClAs	67	130-132	.2286	14.28	22.26	22.67
γ-chloropropyl-(2-methyl-5-arson	-						
ophenyl)-	C11H15O5NClAs	72	160-162				

3-p-Arsonophenyl-2-oxazolidone, (p)H₂O₃AsC₅H₄NCOOCH₂CH₂.—A mixture of

24 g. of  $\beta$ -chloro-ethyl-(p-arsonophenyl) carbamate with 150 cc. of water and 5.9 g. (2 molecular equivalents) of sodium hydroxide was refluxed for 5 hours. At the end of that time the solution was cooled and concd. hydrochloric acid added until the mixture

was strongly acid to congo red; this caused the solution of any amino-alcohol which might have formed as a by-product during the reaction, and at the same time caused the precipitation of the oxazolidone. The product was filtered, washed with water and purified by crystallization from 30% acetic acid. There was thus obtained 20 g. (95%) of colorless plates melting above 280°.

Analysis. Subs., 03178: 22.36 cc. of 0.0963 N I2. Calc. for C9H10O5NAs: As, 26.13. Found: 25.54.

3-o-Arsonophenyl-2-oxazolidone, (o)H2O3AsC6H4NCOOCH2CH2.—A mixture of

2.1 g. of β-chloro-ethyl-(o-arsonophenyl) carbamate with 2.6 cc. (2 molecular equivalents) of 5 N sodium hydroxide and 20 cc. of water was refluxed for 3 hours. The solution was cooled and acidified with coned. hydrochloric acid until strongly acid. The product separated as a white powder which was purified by crystallization from 20% acetic acid. There was thus obtained 1.3 g. (69%) of colorless plates melting at 212-213° with decomposition.

Analysis. Subs., 0.3630: 25.63 cc. of 0.0963 N I2. Calc. for C9H10O5NAs: As, 26.13, Found: 25.63.

3-p-Arsonophenyl-1,3,2-oxazone, (p)H2O3AsC6H4NCOOCH2CH2CH2.--A mixture

of 4.2 g. of  $\gamma$ -chloropropyl-(p-arsonophenyl) carbamate with 20 cc. of boiling absolute alcohol and 14 cc. (2 molecular equivalents) of a 10% solution of potassium hydroxide in absolute alcohol was refluxed for 2.5 hours. A granular precipitate of potassium chloride started to form at the very beginning and increased in amount until the end of the time mentioned. The mixture was cooled, the granular precipitate filtered off, and hydrogen chloride passed into the alcoholic filtrate until it reacted strongly acid. The solvent was then evaporated and the sol d residue combined with the original precipitate. By treatment of the total solid with dil. sodium hydroxide solution in the cold, the potassium chloride and sodium chloride dissolved, and the product was readily precipitated with an excess of hydrochloric acid. It was purified by crystallization from dil. acetic acid, yielding 2.8 g. (72%) of white plates which melted at 245-247° with decomposition.

Analysis. Subs., 0.2007: 13.52 cc. of 0.0963 N I2. Calc. for C10H12O5NAs: As, 24.58. Found: 24.43.

Arsono-arylamino-ethanols and -propanols.—A  $\beta$ -chloro-ethyl- or  $\gamma$ -chloro-propyl-(arsono-aryl) carbamate was dissolved in 10% aqueous sodium hydroxide containing 5 molecular equivalents of alkali. The solution was refluxed for 4 hours, cooled, and coned, hydrochloric acid added until the mixture was neutral to congo red. The aminoalcohols separated usually as white solids but occasionally as oils which solidified on

TABLE II ETHANOLS AND PROPANOLS

				Obt. or	ysis		
Substance Formula	Yield %	М. р. °С.		req. Cc. of 0963 N	Calc.	Found	
β-(p-arsonophenyl)-amino-ethanol C ₈ H ₁₂ O ₄ NAs'	85	173-174	0.3039	23.53	28.78	28.11	
β-(c-arsonophenyl)-amino-ethanol C ₈ H ₁₂ O ₄ NAs	50	144-146	. 3630	28.26	28.74	28.26	
β-(2-methyl-5-arsonophenyl)-amino-							
ethanol CoH14O4NAs		144-146	.2314	17.88ª	27.09	26.89	
γ-(p-arsonophenyl)-amino-propanol C9H14O4NAs	87	167-168	. 2025	15.17	27.09	27.21	
γ-(0-arsonophenyl)-amino-propanol C3H14O4NAs	66	84-85	.2108	15.62	27.09	26.81	
γ-(2-methyl-5-arsonophenyl)-amino-					구함하다		
propanol C ₁₀ H ₁₆ O ₄ NAs		142-143	.2053	15.214	25.95	25.78	
● 0 0928 W To used	FACTURE 1						

standing. The products were filtered, washed with cold water and recrystallized from water. The amino-alcohols thus produced are readily soluble in dil. hydrochloric acid.

They may be formed also by hydrolysis of the corresponding oxazolidone or oxazone but the isolation of these intermediate products is quite unnecessary.

p-Arsonophenyl-β-hydroxyethyl Nitrosamine, (p)H₂O₃AsC₆H₄N(NO)CH₂CH₂-OH.—To a solution of 3.5 g. of β-p-arsonophenyl-amino-ethanol in 6 g. of concd. hydrochloric acid and 6 cc. of water was added a solution of 2 g. of sodium nitrite in 10 cc. of water, with stirring and the mixture then heated to boiling. While still hot it was made alkaline to litmus by addition of 10% sodium hydroxide solution, then cooled and concd. hydrochloric acid was added until the solution was just acid to congo red. A crystalline precipitate separated which was purified by crystallization from water. It formed bright yellow needles which started to darken at 170–175° and melted at 236° with decomposition.

p-Arsonophenyl- $\gamma$ -hydroxy-propyl Nitrosamine, (p)H $_2$ O $_3$ AsC $_6$ H $_4$ N(NO)CH $_2$ CH $_2$ -CH $_2$ OH.—This substance was prepared in a manner exactly analogous to that used for the nitrosamine described above, and formed yellow crystals which were purified from water and melted at 142–143°.

These nitroso compounds gave the expected nitroso-amine reactions.

#### Summary

- 1. Various amino-aryl-arsonic acids were condensed with  $\beta$ -chloro-ethyl- and  $\gamma$ -chloropropyl chloroformates to form the corresponding  $\omega$ -chloro-alkyl-(arsono-aryl) carbamates.
- 2. By treatment with 2 molecular equivalents of aqueous alkali, the  $\beta$ -chloro-ethyl-(arsono-aryl) carbamates were converted into arsono-aryl oxazolidones and the  $\gamma$ -chloropropyl-(arsono-aryl) carbamates into 3-arsono-aryl-1,3,2-oxazones.
- 3. By treatment with excess of aqueous alkali the arsono-aryl-oxazolidones or  $\beta$ -chloro-alkyl-(arsono-aryl) carbamates were converted into arsono-aryl-amino-ethanols and the  $\beta$ -arsono-aryl-1,3,2-oxazones or  $\gamma$ -chloropropyl-(arsono-aryl) carbamates into  $\gamma$ -arsono-aryl-amino-propanols. The arsono-aryl-amino alcohols were much less toxic than the corresponding arsanilic acids.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND BIOLOGY OF THE STATE UNIVERSITY OF MONTANA]

# THE ANTISEPTIC ACTION OF THE ZINC CHLORIDE SALT OF

By J. W. Howard and F. D. Stimpert Received October 9, 1923

#### Introduction

In connection with the investigation of the use of zinc chloride as a condensing agent in the preparation of anilides our attention was called to the fact that the chemical and physical data in the literature² concerning a possible side product of the reaction, namely the double salt of aniline with zinc chloride  $[(C_6H_5NH_2)_2\ ZnCl_2]$ , were very meager.

This salt further interested us in that it offered an opportunity to compare the bactericidal action of a compound with its constituent compounds.

The medicinal use of zinc chloride is generally that of an antiseptic or disinfectant, being applied either as a solid or in solution.

While aniline has not been used for these purposes, the fact that it is a compound of known toxicity suggested that a study of its bactericidal action might be of value as well as a comparison of this action with that of zinc chloride and with its double salt with zinc chloride.

In order to make the data concerning the salt of aniline with zinc chloride more complete as well as to make the bactericidal comparisons mentioned the following study has been carried out.

# Experimental Part

Zinc Chloride.—Fused, U. S. P. sticks of commercial quality were used in making the solution.

Aniline.—The usual constant-boiling fraction of freshly distilled aniline was used.

Zinc Chloride Salt of Aniline.—Ten g. of aniline was thoroughly mixed with 7.5 g. of finely ground, fused zinc chloride. This mixture was allowed to stand for one hour after the heat of the reaction had subsided. The reaction product was extracted with boiling 95% alcohol, from which the salt readily crystallized on cooling; yield, 11 g.

The needles soften slightly at 230° and melt at 255°. The salt is soluble to the extent of 0.64 g. in 100 cc. of water at 20°; 0.87 g. in 100 cc. of 0.4% hydrochloric acid at 20°; 0.066 g. in 100 cc. of 95% alcohol at 20°. It is also only very slightly soluble in carbon disulfide, chloroform, benzene or ethyl ether. It is somewhat more soluble in methyl alcohol or acetone. It is slowly decomposed by 3 N sodium carbonate solution, readily by 1 N

¹ Presented before the Division of Chemistry of Medicinal Products at the 66th meeting of the American Chemical Society, Milwaukee, Sept. 10-14, 1923.

² Schiff, Jahresber., 1863, 413. Lachowicz and Bandrowski, Monatsh., 9, 512 (1888). Tombeck, Compt. rend., 124, 961-3 (1897). Base, Am. Chem. J., 20, 646 (1898). Hodges, Chem. News, 103, 52 (1911). Reddelien, Ann., 388, 165 (1912).

sodium hydroxide or boiling water. The water solution becomes slightly cloudy on standing for several days at room temperature.

Calc. for C₁₂H₁₄N₂ZnCl₂: N, 8.71. Found: 8.72, 8.75.

Bactericidal Studies.—For this purpose a 6% solution of zinc chloride, a 3% solution of aniline and a 0.6% solution of the zinc chloride salt of aniline were used. The latter two solutions were made in these concentrations because of their limited solubilities in water. The zinc chloride solution was made stronger than the others, as preliminary experiments indicated that this was necessary for comparative purposes.

These solutions were so diluted as to make a total of 5 cc. in each case. To each of these portions of 5 cc. was added 0.1 cc. of a 24-hour broth culture of staphylococcus aureus that had been transplanted on 2 successive days. At 5-minute intervals a 5mm. loop was transplanted from these solutions in 10 cc. of broth and incubated for 48 hours. An examination was made of the broth for positive and negative cultures by cloudiness. These results were then checked by plating 1 cc. of the 48-hour broth culture and incubating for 48 hours. These results were further checked by direct plating from the bacteria suspensions in the original solutions and incubating.

Table I
RESULTS
6% Zinc chloride solution

Dilutions Cc. soln.	Cc. water	ŏ	Time in	minutes	20
5				_	
4	+1	+	+ +	+	
2.5	+2.5	+	+	+	+ (few)
2	+3	+ .	+	+	+ (few)
0.5	+4.5	+	+	+	+
		3% Aniline s	olution		
5			-		
4	+1	+		-	_
3	+2	+	+ 1	-	
2	+3	1 +	+ +	+	
1	+4	+	+	+	+

This would indicate that aniline has about four times the disinfectant power of zinc chloride in solution.

TABLE II

0.6% Solution of zinc chloride salt of aniline
5 cc. of solution

Time in minutes	5 10	15 20	25 30	35
Results	+ +	+ +	+ -	
	(strong) (strong)	(mod.) (few)	(few)	

As this table indicates, there would be no object in diluting this solution further. The colony counts here indicated a gradual but marked decrease

with increase in time. The 15- and 20-minute plates on comparison with the aniline and zinc chloride plates of the same times and dilution show clearly a stronger antiseptic action. Predicting from the curve obtained from the aniline solution, in order to compare on a time basis with the salt solution, the results would seem to indicate that the salt has about 1.3 times the disinfecting power of aniline and about 5 times that of zinc chloride.

When the salt solution was allowed to stand for a week at room temperature, it became somewhat cloudy and lost the power to kill the bacteria in even the 30- or 35-minute periods.

#### Summary

- 1. The double salt of aniline with zinc chloride has been prepared and physical and chemical data have been added to those already existing.
- 2. Its bactericidal action has been found to be greater than that of either aniline or zinc chloride.

MISSOULA, MONTANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES.¹ V. THE USE OF ACETYLENE FOR THE SYNTHESIS OF CYCLIC ACETALS

By Harold S. Hill² and Harold Hibbert Received October 16, 1923

In a previous communication³ the authors have pointed out the structural relationship existing between cyclic acetals and polysaccharides, that is, that the carbonyl-hydroxyl condensation reaction involved in cyclic acetal formation is without doubt duplicated, either inter- or intramolecularly, or both, when simple sugars condense to form di-, tri-, or polysaccharides. In view of this relationship the belief was expressed that a thorough investigation of the simpler cyclic derivatives would afford a promising means of attack for the problem of the nature of the complex molecules of starch, inulin, cellulose, etc. It is in the course of this work that a new and improved method for the synthesis of cyclic acetals has been developed.

Earlier investigators have prepared cyclic acetals from acetaldehyde and ethylene glycol,⁴ trimethylene glycol,⁴ 1,2-propylene glycol,⁵ glycerol,⁶

- ¹ The title has been altered so as to be more in accord with present, and proposed future investigations (Hibbert).
  - ² Antoine Chiris Co. Research Fellow.
  - 3 Hibbert and Hill, This Journal, 45, 734 (1923).
- ⁴ (a) Würtz, Compt. rend., **53**, 378 (1861); Ann., **120**, 328 (1861); (b) Lochert, Ann. chim. phys., [6] **16**, 26 (1889). (c) Clark, J. Chem. Soc., **101**, 1803 (1912).
  - ⁵ Gramont, Compt. rend., 97, 173 (1883); Bull. soc. chim., 41, 361 (1884).
  - . 6 Harnitzky and Menschutkin, Ann., 136, 126 (1865).

and mannitol,⁷ by heating mixtures of acetaldehyde (or paracetaldehyde) and polyhydroxy derivatives, either alone or with a catalyst which was usually hydrochloric, sulfuric, or phosphoric acid, or iodine.⁸

In a number of interesting researches, Nieuwland and co-workers^{9,10} have recently shown that various condensation reactions between acetaldehyde and other products (aniline, toluidine, methyl alcohol, ethyl alcohol) take place as well, or better if, instead of using the free aldehyde, this is generated *in situ* from acetylene, catalytically, by the agency of a small amount of a mercuric salt in the presence of sulfuric acid. Thus, by passing the gas into a mixture of an alcohol and the catalyst it was possible to synthesize the simple acetals.

In view of this, it seemed highly probable that the same process might be applied to the preparation of *cyclic* acetals, and it has, in fact, been found that not only are high yields of uniformly pure products more easily and cheaply obtainable at room or moderate temperature, and in a much shorter time by this method, but it is now possible to synthesize readily a number of cyclic acetals, the preparation of which is rendered difficult, and in some cases even precluded, by the unfavorable experimental conditions associated with the earlier methods of formation.¹¹

The procedure used consists essentially in passing acetylene with vigorous stirring into a mixture of a polyhydroxy compound and a small amount of mercuric sulfate and coned. sulfuric acid (93%) as a catalyst. It has been applied with good results to the synthesis of cyclic ethylidene derivatives of ethylene glycol, trimethylene glycol, 1,2-propylene glycol, 1,4-tetramethylene glycol, glycerol- $\alpha$ -bromohydrin, glycerol, 2,3-dimethyl-2,3-butanediol (pinacol), 2-methyl-2,4-pentanediol, and  $\alpha$ -methyl glucoside. Attempts to obtain a similar product from glucose yielded a sirup which could not be crystallized or distilled, but which gave every indication of being an acetal.

Of the above derivatives, ethylidene glycerol was prepared by Harnitzky and Menschutkin⁶ in 1865 by heating glycerol and acetaldehyde together

- ⁷ Meunier, Compt. rend., 107, 910 (1888).
- ⁸ Hibbert, This Journal, 37, 1762 (1915).
- 9 Vogt and Nieuwland, ibid., 43, 2071 (1921).
- 10 Reichert, Bailey and Nieuwland, ibid., 45, 1552 (1923).
- 11 The possibility of synthesizing cyclic acetals by the use of acetylene was suggested to Dr. J. A. Nieuwland by the writer some eighteen months ago. He was kind enough to intimate that in view of our greater interest in this particular phase of the subject he would be glad to see the work carried out by us. We desire to express to him and his co-worker, Mr. Hoffmann, our appreciation of the kindness accorded, especially since the latter, due to a misunderstanding, later prepared, independently and almost simultaneously with ourselves, one or two identical acetals, namely, those from trimethylene glycol and pinacone.

In further agreement, and with Dr. Nieuwland's kind consent, it is our intention to extend his acetylene method to the synthesis of cyclic acetals from polyglycols.

at 180° in a sealed tube. Their product boiled at 184–188° and was only slightly soluble in water, whereas the ethylidene glycerol obtained by the new acetylene method boils at 189–195° and is miscible with water in all proportions. Nef¹² also obtained an ethylidene glycerol, soluble in water. It is to be noted in this connection that somewhat the same discrepancies exist between the benzylidene glycerol described by Harnitzky and Menschutkin and that prepared later by Fischer,¹³ and also by Irvine, Macdonald and Soutar.¹⁴ It is probable that in both cases the earlier investigators were dealing with impure products. The question as to whether ethylidene glycerol exists as a 5- or a 6-membered cyclic structure will be taken up in a later paper.

The cyclic acetals of 2,3-dimethyl-2,3-butanediol (pinacol) and of its isomer 2-methyl-2,4-pentanediol, representing 5- and 6-membered rings, have not been obtained previously. Their synthesis by the acetylene method is noteworthy in that the ethylidene cyclization takes place in preference to dehydration and rearrangement to pinacolone derivatives, in spite of the presence of concd. sulfuric acid which presumably should tend to favor the two latter reactions. Both of these acetals are colorless, volatile liquids having a strong odor of camphor and menthol.

The cyclic acetal of 1,4-tetramethylene glycol, I, is also of interest in that it represents a new type of comparatively rare 7-membered ring. 15

The existence and ease of formation of this acetal would seem to indicate that speculations regarding the structure of polysaccharides are by no means limited to the probabilities of only five- and six-membered heterocyclic groups.

- 12 Nef, Ann., 335, 216 (1904).
- 13 Fischer, Ber., 27, 1536 (1894).
- ¹⁴ Irvine, Macdonald and Soutar, J. Chem. Soc., **107**, 344 (1915).
- ¹⁵ As far as can be ascertained this is the only known example of a simple, saturated, heterocyclic structure containing 5 carbon and 2 oxygen ring atoms. In fact, the only 7-membered heterocyclic carbon-oxygen derivatives of any kind appear to be the ε lactone, 2-6-dimethyl-octane-carboxylic-acid-3,8-olid, and its isomer, 5-isopropylheptane-carboxylic-acid-2,7-olid, both isolated by Baeyer and his co-workers [Ber., 29, 29 (1896); 32, 3619 (1899); 32, 3629 (1899); 33, 860 (1900)].

So far as the authors are aware, the crystalline ethylidene product (m. p., 77°) from  $\alpha$ -methyl glucoside is the first acetaldehyde derivative of a sugar to be described, although various benzaldehyde¹⁶ and acetone¹⁷ derivatives of carbohydrates are known. By analogy with other derivatives this ethylidene product presumably has the structure II. The benzylidene derivative of  $\alpha$ -methyl mannoside contains two aldehyde residues, and it is therefore to be expected that diethylidene  $\alpha$ -methyl mannoside will result from the treatment of this glucoside with acetylene. ¹⁸

In the adaptation of the acetylene method of cyclic acetal formation to solid polyhydroxy compounds, such as pinacol,  $\alpha$ -methyl glucoside, and glucose, it was found advantageous to use ethylene glycol as a solvent. The treatment of the solution with acetylene yielded a mixture of the acetals of both the solvent and solute from which the two components were readily separated by distillation.

#### Mechanism of the Reaction

There is no conclusive evidence with regard to the mechanism of the reaction involved in the formation of cyclic acetals from acetylene, although there are two likely possibilities. The first is that acetylene in the presence of mercury salts reacts with traces of water to form acetaldehyde, which in turn condenses with the polyhydroxy compound with regeneration of water. An objection to this scheme lies in the fact that it involves a simultaneous hydration and dehydration which, while not unknown, is hardly plausible, and further that the amount of water present would appear to be too small to account for the rapidity of the reactions, in view of the strong attraction of the acid for it. In every case anhydrous glycols were used, only a small amount of concd. sulfuric acid was added, and the acetylene itself was bubbled through concd. sulfuric acid before it entered the reaction vessel.

A second and more probable alternative is that a direct addition reaction occurs between acetylene and the glycol used. Leaving out of consideration the catalytic role of the mercury salt, for which Nieuwland has postulated an intermediate molecular complex, it would appear that the majority of these acetylene reactions consist essentially in the addition, through the oxygen atom, of an hydroxyl derivative to an unsaturated carbon atom of acetylene with subsequent rearrangement. In the case where dil. sulfuric acid is employed, acetaldehyde is formed, the hydroxy compound in this case being water.

¹⁶ Irvine and Scott, J. Chem. Soc., 103, 575 (1913).

¹⁷ Macdonald, ibid., 103, 1896 (1913).

¹⁸ It is our intention to extend the investigation to other carbohydrates and polysaccharides.

Acetaldehyde

·· -> shows the relative direction of free partial valence force.

With a glycol replacing water in the series of changes given above, similar reactions occur, first, *intermolecularly* between acetylene and one hydroxyl group, and second, *intramolecularly* with the other hydroxyl, the whole transformation being practically instantaneous.

> > Ethylidene ethylene glycol

As to the actual changes which render the acetylene capable of effecting such "addition" reactions, it is possible that these may take place in three stages: (1) the formation of an acetylene-mercury derivative; (2) decomposition of this with removal of the mercury and addition of the elements of sulfuric acid; (3) removal of sulfuric acid and addition of water or glycol.¹⁹

Possibly a similar addition and rearrangement may take place in a variety of reactions involving hydroxyl derivatives, for example: in ester and anhydride formation, etc.

# **Experimental Part**

# Description of Apparatus

Acetylene was supplied from a commercial tank, the gas being first passed into a gasometer in order to afford a means of pressure control and volume measurement.

¹⁹ The fact that dry acetylene can condense directly with anhydrous amines and alcohols, in the presence of concd. sulfuric acid, has been shown by Nieuwland and coworkers. (Refs. 9, 10.)

The arrangement used consisted in mounting two 20-liter glass bottles (having openings at both top and bottom), one above the other. The outlets near the bottom of both were connected by means of heavy rubber tubing, and the securely attached stopper of the lower vessel contained the inlet from the acetylene tank, as well as the outlet leading to the reaction flask, both of these connections being equipped with stopcocks. After the lower bottle was filled with water and this forced into the upper one by means of acetylene from the tank, the valve of the latter was closed, as well as the stopcock on the inlet in order to prevent any leakage taking place through the connection on the tank. An opening to the atmosphere was left in the top of the upper bottle, and in filling the gasometer with acetylene care was taken to admit the gas from the high-pressure tank cautiously and only when the proper stopcocks were open. The amount of gas used was determined from the readings on the lower bottle, this having been calibrated for temperature and pressure to give directly the volume under standard conditions.

From the gasometer the acetylene was passed through a single wash bottle containing concd. sulfuric acid, and from this into the reaction vessel. The latter, in the majority of the experiments described later, was a large-neck, 2-liter, round-bottom flask, having a well-fitted rubber stopper through which passed an inlet tube extending nearly to the bottom of the flask, an outlet tube near the top equipped with a stopcock and a mechanical stirrer. The stirring device operated through a mercury seal, deep enough to hold the maximum gas pressure employed (about 5 cm. of mercury) and was designed to produce a splashing effect so as to insure an efficient mixing of gas and liquid.

#### Description of Method

The preparation of ethylidene ethylene glycol may be taken as illustrative of the acetylene method of synthesizing cyclic acetals.

Four g. of mercuric sulfate was triturated in a mortar with 4 cc. of ordinary concd. sulfuric acid (93%), the resulting paste transferred to 62 g. of pure ethylene glycol while the mixture was cooled and shaken, and the whole then poured into the reaction flask. The stopcock on the outlet tube of the latter was opened and the air in the apparatus displaced by acetylene. The outlet was then closed, the contents vigorously stirred, and acetylene led in under the full pressure of the gasometer. Absorption started at once and the rate increased rapidly as the reaction mixture became less viscous due both to the spontaneous rise in temperature and the progressive transformation of glycol into its acetal.

In the preparation of the majority of cyclic acetals the temperature could be allowed to rise with safety to  $60-70^{\circ}$ , but in the case of such compounds as pinacol,  $\alpha$ -methyl glucoside, etc., it was advisable to operate at a lower temperature, not higher than  $10-25^{\circ}$ , and to use a cooling bath. The time required for the absorption of the calculated amount of acetylene was in general about 30 minutes, this varying somewhat with the nature of the glycol, the temperature used, and the viscosity of the material.

When the required amount of acetylene had been run in, the stirrer was stopped, the flow of gas cut off, the reaction mixture transferred at once to another flask, and the residue washed out with ether. More ether was added and the combined ether solutions were washed once with a 10%

solution of sodium carbonate to neutralize any sulfuric acid present. Since a number of cyclic acetals are soluble in water it is advisable to use as little of the carbonate solution as possible and to extract the wash liquor once or twice with ether. The combined ether solution was dried over solid potassium carbonate, and fractionated through a 30cm. bead column to remove the solvent. In this way 66 g. of ethylidene ethylene glycol, b. p. 82–85°, was obtained. Except for small traces of other derivatives, this was the sole product formed in the reaction. The yield obtained, calculated on the weight of glycol taken, was equal to 75%.

Experiments carried out, using concd. sulfuric acid (93%) to which several per cent. of water had been added, resulted in decreased yields of the ethylidene derivative and the formation of objectionable by-products. Larger amounts of the pure concentrated acid did not favor the yield, and four times the amount employed as above produced considerable charring during the reaction.

Preparation of Ethylidene Trimethylene Glycol. III.—One hundred and fourteen g. of trimethylene glycol gave 115 g. of the cyclic acetal; b. p., 108–111°; yield, 75%. The absorption of gas took place even more rapidly than in the case of ethylene glycol. There were no by-products.

Preparation of Ethylidene 1,2-Propylene Glycol. IV.—One hundred and fourteen g. of glycol yielded 106 g. of the acetal; b. p.,  $92^{\circ}$ ; yield, 70%.

Preparation of Ethylidene Glycerol Bromohydrin. V.—One hundred and fifty-five g. of pure glycerol- $\alpha$ -bromohydrin, b. p. 132° (15 mm.), gave 85 g. of the corresponding cyclic acetal; b. p., 170–182°; yield, 40%. In this experiment the absorption of acety-lene became very slow after about one-half of the calculated amount had been added, and finally ceased altogether. In the ether extract there was a considerable quantity of a higher boiling material which could not be distilled. The bromine atom in the molecule appears to hinder the reaction with acetylene, since the same difficulty was encountered with other bromine derivatives. Ethylidene bromohydrin, however, may be easily prepared with a 70% yield by heating  $\alpha$ -bromohydrin with paracetaldehyde and a trace of iodine as catalyst.³

Preparation of Ethylidene Glycerol. VI or VII.—One hundred thirty-eight g. of glycerol (anhydrous) gave 110 g. of ethylidene derivative; b. p., 189–196°; yield, 63%. In this preparation efficient stirring was rendered difficult on account of the high viscosity of the glycerol, and this resulted in a decrease in the rate of absorption of the acetylene. It was found, however, that by surrounding the reaction flask with a water-bath maintained at about 70°, the speed of the reaction was greatly increased without the produc-

tion of any injurious effect, and in this way the required 34 liters of gas was absorbed in  $1^{1}/_{2}$  hours.

Ethylidene glycerol as prepared by this method, is a colorless, limpid sirup, completely miscible with water, ether, and alcohol. It has only a slight odor when freshly prepared but on standing, especially in moist air, acquires the odor of acetaldehyde. It is hydrolyzed into glycerol and acetaldehyde by dilute acids.

Preparation of Ethylidene 1,4-Tetramethylene Glycol. VIII.—Owing to the small quantity of tetramethylene glycol available because of the difficulties involved in its preparation, this experiment was performed on a small scale. Eighteen g. of the glycol was treated with 4.6 liters of acetylene, using 0.6 cc. of concd. sulfuric acid and 0.8 g. of mercuric sulfate as a catalyst. The addition of the acetylene required several hours, the slow rate of absorption being due to some extent to the inability to stir such a small amount of material efficiently. The ether extract after two fractionations gave 4.6 g. of a colorless liquid, b. p.  $125-127^{\circ}$ , equivalent to a 20% yield. In the flask there remained an equal amount of a thick sirup which could not be distilled but gave every indication of being an acetal, as it yielded acetaldehyde on treatment with acids, etc.

The product boiling at 124–127°, namely, ethylidene tetramethylene glycol, has the same characteristic odor as the cyclic acetals from ethylene and trimethylene glycols, as well as the same general physical and chemical properties. Its boiling point is also in harmony with those of the corresponding acetals from ethylene and trimethylene glycols.

Analyses. Calc. for C₆H₁₂O₂: C, 62.94; H, 10.3. Found: C, 60.9; H, 9.97.

The low value for carbon was doubtless due to a slight amount of impurity, which it was not possible to remove from the acetal due to the small amount of material available for fractionation. The low yield was also due to some extent to the small weight of glycol used, since a parallel experiment on the same scale with ethylene glycol gave a relatively small yield of the corresponding acetal.

Preparation of Ethylidene Pinacol. IX.—Twenty g. of pinacol prepared from pinacol hydrate by dehydrating it over concd. sulfuric acid was dissolved in 30 g. of ethylene glycol, and the solution treated as usual with 16 liters of acetylene, using as catalyst 3 g. of mercuric sulfate and 3 cc. of concd. sulfuric acid. The temperature was kept below 20°, about 1½ hours being required for the absorption of the gas. Careful fractionation of the reaction product gave (a) ethylidene ethylene glycol, 35 g., yield 81%; and (b) ethylidene pinacol, 15 g., b. p. 133-134°; yield, 61%.

Analyses. (b) Calc. for C₈H₁₆O₂: C, 66.66; H, 10.97. Found: C, 66.22; H, 10.97.

The pinacol derivative, unlike the acetals from ethylene, trimethylene and tetramethylene glycols, is only slightly soluble in water, but resembles them in its other properties. It possesses a powerful, camphor-like odor.

Synthesis of Ethylidene 2-Methyl-2,4-Pentanediol. X.—Twenty-nine g. of the glycol²⁰ and the corresponding amount of catalyst, on treatment with 5.6 liters of acetylene gave 27 g. of ethylidene derivative, b. p. 139-140°; yield, 71%. Its properties were almost identical with those of the isomeric ethylidene pinacol.

Analyses. Calc. for C₈H₁₆O₂: C, 66.66; H, 10.97. Found: C, 66.62; H, 11.08.

Synthesis of Mono-ethylidene- $\alpha$ -methyl Glucoside,—Twenty g. of  $\alpha$ -methyl glucoside was dissolved in 80 g. of ethylene glycol, 4 g. of mercuric sulfate and 3 cc. of

²⁰ This glycol was supplied through the kindness of Dr. R. R. Read of the University of Vermont, to whom we wish to express our best thanks.

coned. sulfuric acid were added, and the mixture was treated with 34 liters of acetylene. The temperature was kept below 10° to prevent decomposition of the glucoside by the acid present. As a result of the low temperature the rate of absorption was somewhat slower than in the synthesis of the ethylidene glycols. After the completion of the reaction, ether containing a little absolute alcohol was added, the solution washed with a small amount of a concentrated solution of potassium carbonate, filtered, and then dried over the solid carbonate. The solvents (including ether, alcohol, and the ethylidene glycol formed in the reaction) were removed by distillation, first under atmospheric, and during the later stage, under diminished pressure, in order to maintain a temperature below 60° throughout the operation. The resulting sirup was freed from the last traces of solvents by being kept several days in an evacuated desiccator. In the first preparation the crystallization started slowly and was brought about by exposing the product to the air on a watch glass and rubbing with a glass rod. When once a sample of the solid product had been obtained, the sirups were readily crystallized by "seeding." The crude product was recrystallized from ligroin containing a small amount of dry ether, and obtained as silk-like, white crystals; m. p., 77°.

Analyses. Calc. for C9H16O6: C, 49.0; H, 7.27. Found: C, 48.4; H, 7.22.

Synthesis of Ethylidene Glucose.—The same procedure as used in the preparation of ethylidene- $\alpha$ -methyl glucoside was applied to glucose.²¹ A nearly colorless, very sticky, ether-soluble sirup was obtained which, however, could not be crystallized. It was readily hydrolyzed by means of dilute acids to glucose and acetaldehyde. The sirup was not analyzed.

#### Summary

- 1. A new method has been developed for the preparation of cyclic acetals from polyhydroxy compounds. This consists in passing acetylene gas into the hydroxy derivative (containing a small amount of mercuric sulfate and concd. sulfuric acid, 93%) at room, or at a moderate temperature.
- 2. In the case of solid hydroxy derivatives (pinacol, glucosides, etc.), these are first dissolved in glycol and the resulting ethylidene derivatives then separated by a simple distillation process.
- 3. The mechanism of the reaction possibly consists, at least in part, of an *inter*molecular addition of the glycol to the acetylene, followed by a rearrangement, this being succeeded in turn by an *intra*molecular addition, followed by a second, subsequent rearrangement.

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²¹ It was observed that pure, dry, powdered glucose when merely mixed with glycol apparently undergoes some physical or chemical change, in that the product sets to a stiff paste, or, with a larger proportion of the glucose, to a solid mass. The phenomenon is being investigated.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. VI. RELATIVE EASE OF FORMATION OF FIVE- AND SIX-MEMBERED HETEROCYCLIC CARBON-OXYGEN CONFIGURATIONS

By Harold S. Hill¹ and Harold Hibbert Received October 16, 1923

There is probably no more general characteristic of all varieties of sugars and polysaccharides than the recurrence in one form or another of heterocyclic, carbon-oxygen configurations. At the present time, however, the greatest confusion exists concerning the relative stability and ease of formation of the different cyclic structures encountered, so that any evidence of a general character which can be brought forward regarding either of these factors is of importance from both theoretical and practical standpoints. A large amount of work will have to be done before the solution of such a complicated problem may be hoped for, and it is obvious that at the present early stage of the investigation it is desirable first to ascertain the relationships existing between the simplest possible derivatives. The present research is concerned mainly with supplying evidence concerning the relative ease of formation of the ring systems A and B, using for this purpose "partition experiments" by the

new acetylene method for the synthesis of cyclic acetals described in the preceding communication,² (Part V). This consists essentially in passing acetylene into a glycol mixed with a small amount of concd. sulfuric acid and mercuric sulfate, the latter acting as a catalyst.

The "partition principle," as applied to this reaction, is based on the assumption that, when one molecular weight of acetylene is passed into a mixture of one molecular weight of each of two different glycols, the gas will react preferentially, and consequently the amounts of the two cyclic acetals formed will be a relative measure of their ease of formation. The reaction would appear to be admirably suited for such a study since, (1) only traces of by-products are formed; in other words, the acetylene

- ¹ Antoine Chiris Co. Research Fellow.
- ² This Journal, 45, 3108 (1923).
- Michael, J. prakt. Chem., N. F., 60, 341 (1899); Ber., 39, 2138, 2143, 2149, 2153, 2157, 2569, 2785, 2789 (1906); 40, 140 (1907).

reacts only to form cyclic acetals; (2) there is practically no hydrolysis of the acetals to acetaldehyde and glycol, only traces of water being present throughout the reaction; there was also little, or no darkening, indicating the absence of free aldehyde; (3) there is no reverse reaction; (4) the acetylene is supplied only as fast as it reacts.

The objection might be raised that different solubility relationships between the two glycols and their respective acetals might bring about a preferential reaction with the acetylene. Against this view is the fact that, in the experiments on which the conclusions of this paper are based, the materials used, and the products formed, were either all mutually soluble, thereby insuring the presence of one phase throughout, or else their solubilities were so nearly identical as to render it unlikely that a given reaction would be appreciably favored by this factor.

#### Discussion of Experimental Results

In reviewing the evidence it is well to bear in mind the three main factors governing the ease of ring formation in this type of reaction.⁴

⁴ In this connection mention should be made of the investigations of Boeseken in which he attempts to show that the ease of formation of cyclic structures by the interaction of an aldehyde or acetone with a polyhydroxy derivative is dependent largely on the relative spatial positions of the hydroxyl groups about the carbon axis. Such a reaction, it is claimed, takes place readily only when the two hydroxyls involved are on adjacent carbon atoms, and on the same side of the chain. He had previously shown [Ber., 46, 2612 (1913)] that compounds having this configuration, when added to a solution of boric acid, increase its conductivity, and from the results of experiments using this method, concluded that in the simple glycols, such as ethylene, trimethylene and tetramethylene glycol, pinacol, etc., the two hydroxyls are on opposite sides of the chain, while in glycerol and many other polyhydroxy compounds there are two on the same side. He then determined [Rec. trav. chim., 40, 525 (1921)] the equilibrium constants for the reaction of acetone with ethylene glycol, chlorohydrin and glycerol, and found values of K equal to 0.28, 0.14 and 0.77, respectively, thus proving, in his opinion, the marked influence exerted on the ease of ring formation by the spatial position occupied by the hydroxyl groups. A serious objection must be raised to such evidence in that Boeseken, in drawing conclusions from his determinations of equilibrium constants, has apparently disregarded the fact of the widely different energy relationships of the groups H, Cl, and CH2OH, which must in themselves be potent factors in influencing the extent to which the cyclic ketals are formed, and hydrolyzed. It seems rather improbable that the compounds,

would be formed and hydrolyzed with the same ease, regardless of the position of the hydroxyl groups in the free glycol or glycerol. A further objection to Boeseken's view is the ease with which a wide variety of aldehydes react with all the simple glycols, as well as with glycerol and the more complex polyhydroxy compounds. In view of such conflicting evidence, it is considered doubtful that the spatial configuration of the hydroxyl groups in the *simple* 1, 2 and 1, 3 diol derivatives exerts an appreciable influence on the ease of formation of their cyclic acetals.

These are (1) the number of atoms in the ring; (2) the nature of the atoms in the ring; (3) the nature of the atoms or groups attached to the ring atoms.

# Influence on Ring Formation Exerted by the Number of Atoms in the Ring

An experiment involving a partition of acetylene between ethylene glycol and trimethylene glycol showed that the 6-membered cyclic structure, II, is formed in marked preference to that containing 5 ring atoms, I, the ratio being approximately 2:1.

A similar experiment using the isomers, 1,2-propylene and trimethylene glycols, gave almost the same ratio, favoring II over III.

The partition experiment between 2-methyl-2,4-pentanediol and ethylene glycol yielded five times as much of the 6-membered cyclic derivative, IV, as of ethylidene ethylene glycol, I, while when the same experiment was repeated using trimethylene glycol instead of ethylene glycol, the ratio of configuration, IV to that of II, was found to be only about 2: 1. The results of these two experiments, therefore, supply indirect, yet clearly confirmatory evidence that it is primarily the structure (size) of the ring itself which determines the greater ease of formation of II over I.⁵

# The Influence of Groups Attached to the Ring Atoms

Partition experiments, using the acetylene method for the synthesis of cyclic acetals, appear to establish the fact that where formation of similar rings is concerned the presence of methyl groups attached to the glycol carbon atoms favors cyclization. Thus, IV is formed in preference to II

⁵ This is in agreement with the earlier work carried out in this Laboratory by Dr. John A. Timm (not yet published), on the "partition ratios" obtained when using one molecular equivalent of an aldehyde with one equivalent each of a 1,2, and a 1,3 glycol and a small amount of sulfuric acid (40%) as a catalyst.

in the ratio of 2:1. Formation of cyclic acetal IV takes place five times as easily as I, while with II and I, which involve the same rings except for the absence in the former of methyl groups, the ratio is only 2:1.

In harmony with such evidence are the observations of Meyer,⁶ Hjelt⁷ and others,⁸ that (a) tetramethyl- and other alkylated succinic acids form cyclic anhydrides with markedly greater ease than succinic acid itself, and that (b) by Evans,⁹ that methylated cyclic oxides are prepared more readily than those having no methyl groups attached to the ring atoms.

On the other hand, cyclic acetal formation is apparently hindered by the introduction of a second methyl group on the ring carbon of the acetal-dehyde residue. The compound V, for example, could not be prepared by the earlier methods for the synthesis of such derivatives, ¹⁰ although Boeseken, Schaefer and Hermans¹¹ have recently isolated it. ¹²

It is well known that the replacement of two hydrogen atoms by oxygen in a carbon-oxygen heterocyclic structure causes a great decrease in stability of the ring.

$$\begin{array}{c|cccc} CH_2-CH_2 & CH_2-C=O & CH_2-C=O \\ & O & & O & O \\ CH_2-CH_2 & CH_2-CH_2 & CH_2-C=O \\ Stable & Less stable & Least stable \\ \end{array}$$

A replacement of hydrogen by hydroxyl appears to bring about a similar change.

- 6 Auwers and Meyer, Ber., 23, 101 (1890).
- ⁷ Hjelt, Ber., 26, 1925 (1897).
- ⁸ Manasse and Rupe, Ber., 27, 1822 (1894). Auwers, Ber., 31, 2112 (1898). Von Bischoff, Ber., 23, 620 (1890). Zelinsky, Ber., 24, 3997 (1891).
- ⁹ Evans, Z. physik. Chem., 7, 337 (1891). See Petrenko-Kritschenko and Konschin, Ann., 342, 51 (1905).
  - 10 Fischer and Pfähler, Ber., 53, 1606 (1920).
  - ¹¹ Boeseken, Schaefer and Hermans, Rec. trav. chim., 41, 722 (1922).
- ¹² It would be interesting to ascertain whether this product V could be prepared by passing allylene (CH₃—C≡CH) into trimethylene glycol in the presence of a mercuric salt. If a positive result were obtained, an experiment employing equimolecular quantities of allylene, acetylene and this glycol should give a partition between V and II, the extent of which would provide definite evidence as to the influence on ease of formation of methyl groups attached to a carbon between two ring oxygens.

The Structure of Ethylidene Glycerol

The greater ease of formation of 6-membered over 5-membered cyclic acetals, in the partition of acetylene between a mixture of 1,2 and 1,3 glycols leads to interesting speculations as to the probable structure of ethylidene glycerol. It has been shown² that this cyclic acetal may be obtained with a yield of 63% by means of the acetylene method, the product boiling within the range  $189-196^{\circ}$ . From the results of partition experiments already mentioned, there is no apparent reason why, in the preparation of the glycerol derivative, there should not be an *intra*molecular partition leading to the formation of configurations VI and VII, with the latter predominating.

With a view to obtaining additional data bearing on this problem, experiments were carried out involving a partition of acetylene between glycerol and ethylene glycol, which gave yields of [VI or VII] and I in a ratio of about 2:1. Using trimethylene glycol and glycerol, the ratio of [VI or VII] to II was a little less than 1:2, and a similar experiment with glycerol and 1,2-propylene glycol showed a marked preference in favor of [VI or VII] over III.

Correlating these results as to their bearing on the configuration of ethylidene glycerol, we find:

- A. If the 5-membered cyclic structure, VI, predominates, it follows from the results of partition experiments that (1) the ease of formation of VI is greater than that of VII; (2) VI than I; (3) VI than III; and (4) that of VI is less than that of II.
- B. If the 6-membered ring, VII, predominates (1') the ease of formation of VII is greater than that of VI; (2') VII than I; (3') VII than III; and (4') that of VII is less than that of II.

Alternative B appears to have the greater weight of supporting evidence. 1', 2' and 3' follow from the generalization that in all the cases investigated,

a 6-membered cyclic ethylidene derivative is formed in preference to a 5-, and 4' is in harmony with the observation that replacement of hydrogen on a ring carbon by hydroxyl causes a decrease in tendency towards cyclization. On the other hand, in A there is no particular evidence favoring 1, 2 and 3.

The conclusion to be drawn from partition experiments, therefore, is that ethylidene glycerol is probably a mixture of VI and VII, with the latter predominating.¹³

It should be borne in mind, however, that *iso* propylidene and benzylidene glycerols, have been shown by Irvine and his pupils ¹⁴ as well as by Fischer ¹⁵ to possess the 5-membered cyclic structures,

Just why these two acetals should have a ring configuration different from that of ethylidene glycerol is not clear, but an explanation may possibly be found in the light of the theory developed by Ingold and Thorpe, ¹⁶ namely, that each group attached to a carbon atom influences the direction of the remaining valence bonds, or forces—the larger groups requiring more space. From this it would follow that the angle  $\alpha$  would be less in VIII and IX than in X, thus accounting for the marked tendency of

acetaldehyde to form the larger ring structure, and also for the fact that acetone does not react readily with trimethylene glycol to give the 6-membered *iso* propylidene derivative, V, while the 5-membered *iso* propylidene ethylene glycol can be readily obtained.

With a methylene group attached to two oxygen atoms, XI, the angle  $\alpha$  would be still larger and, as a matter of fact, methylene glycerol exists in two isomeric forms.¹⁷

#### **Experimental Part**

In each of the following experiments the glycol or glycerol used was pure and dry.

Expt. I. Partition of Acetylene between Ethylene Glycol and Trimethylene Glycol.—A mixture of 93 g. of ethylene glycol and 114 g. of trimethylene glycol was treated

¹³ If this is the case, it is possible that the two acetals may hydrolyze at different rates, which fact would make itself known in the properties of the non-hydrolyzed material. The matter is to be investigated further from this standpoint.

¹⁴ Irvine, Macdonald and Soutar, J. Chem. Soc., 107, 337, 815 (1915).

¹⁵ Fischer, Ber., 27, 1536 (1894); 28, 1167, 2496 (1895).

¹⁶ Ingold and Thorpe, J. Chem. Soc., 107, 1080 (1915); 115, 320 (1919).

¹⁷ Schulz and Tollens, Ann., 289, 29 (1896).

with 33.6 liters of acetylene in the presence of 6 g. of mercuric sulfate and 6 cc. of concd. sulfuric acid. The apparatus and method of procedure were the same as that described in the previous communication.² Special care was exercised in securing as exact a measurement of the gas as possible, and the temperature during absorption was not allowed to rise higher than  $60^{\circ}$ . The final product was extracted with other immediately after the required amount of acetylene had reacted, the resulting lower layer being treated several times with this solvent. The other solution was washed with a small amount of 10% aqueous potassium carbonate, the latter extracted with other, and the combined other solutions were dried over solid potassium carbonate and carefully fractionated using a 30cm. bead column. The product was found to consist almost entirely of other, ethylidene of the glycol (b. p.,  $82-85^{\circ}$ ), and of the ethylene glycol (b. p.,  $107-111^{\circ}$ ), the yields of these two acetals being 40 g. and 91 g., respectively. Calculating the percentage yields on the basis of the total possible amounts of each, it was found that the yield of the ethylene derivative was 30%, and that of the trimethylene derivative was 60%.

It is not claimed that this ratio is more than an approximate measure of the relative amounts of the two cyclic configurations formed by this method, due to the difficulty in this case of separating the cyclic acetals completely.

- Expt. II. Partition of Acetylene between Ethylene Glycol and 1,2-Propylene Glycol.—A mixture of 93 g. of ethylene glycol and 114 g. of 1,2-propylene glycol when treated exactly as in Expt. 1, yielded 100 g. of a mixture of the two corresponding cyclic acetals, boiling within the range 85–91°. It was not possible to separate this mixture into its components which boil at 83° and 92°, respectively.
- Expt. III. Partition of Acetylene between Trimethylene Glycol and 1,2-Propylene Glycol.—From a reaction mixture of 66 g. each of trimethylene glycol, 1,2-propylene glycol and 19 liters of acetylene, involving the same quantities of catalyst as in Expts. I and II and operating under the same experimental conditions, by careful fractionation 45 g. (51%) of ethylidene trimethylene glycol (b. p., 107–111°) and 20 g. (23%) of ethylidene 1,2-propylene glycol (b. p., 92–97°) were obtained.
- Expt. IV. Partition of Acetylene between Ethylene Glycol and 2-Methyl-2,4-pentanediol.—A mixture of 29 g. of the pentane derivative and 15.5 g. of ethylene glycol was allowed to react with 5.6 liters of acetylene in the presence of 1.5 g. of mercuric sulfate and 1.5 cc. of concd. sulfuric acid. The temperature was kept at 20°. Fractionation of the extracted products gave approximately 3 g. (13%) of ethylidene ethylene glycol (b. p., 80-90°) and 22 g. (61%) of ethylidene 2-methyl-2,4-pentanediol, (b. p., 138-140°).
- Expt. V. Partition of Acetylene between Trimethylene Glycol and 2-Methyl-2,4-pentanediol.—A mixture of 29 g. of the pentane derivative and 19 g. of trimethylene glycol with 5.6 liters of acetylene yielded about 6 g. (24%) and 16 g. (44%) of their respective cyclic acetals (b. p., 108-115°, and 138-140°). The amounts of catalyst used were the same as in Expt. IV.

Expt. VI. Partition of Acetylene between Ethylene Glycol and Glycerol.—A mixture of 78 g. of glycerol, 53 g. of ethylene glycol and 19 liters of acetylene with 4 g. of mercuric sulfate and 4 cc. of concd. sulfuric acid gave 52 g. (51%) of ethylidene glycerol (b. p., 189–197°) and 19 g. (25%) of ethylidene ethylene glycol (b. p., 80–90°).

Expt. VII. Partition of Acetylene between Trimethylene Glycol and Glycerol.—A mixture of 79 g. of glycerol, 66 g. of trimethylene glycol and 19 liters of acetylene yielded 27 g. (26%) and 41 g. (47%) of their respective cyclic acetals (b. p., 185–197°, and 106–111°). The quantity of catalyst used was the same as in Expt. VI.

Expt. VIII. Partition of Acetylene between 1,2-Propylene Glycol and Glycerol.—A mixture of 79 g. of glycerol, 66 g. of 1,2-propylene glycol and 19 liters of acetylene, gave 42 g. (40%) of ethylidene glycerol (b. p., 189–196°) and 22 g. (25%) of ethylidene-

1,2-propylene glycol (b. p., 91-96°). There was some difficulty in obtaining a complete separation of the acetals from the unchanged glycols, owing to the mutual solubility of 1,2 propylene glycol and ethylidene glycerol in both ether and the aqueous solution of potassium carbonate used in washing the product. In order to ensure the removal of the unchanged glycol and glycerol, it was necessary to wash the extracted product once with water. This wash liquor undoubtedly contained a certain amount of the soluble ethylidene glycerol so that the actual yield of the glycerol derivative was probably somewhat greater than the amount isolated. There is no doubt, therefore, of the preponderance in this reaction of the formation of this acetal over that of ethylidene-1,2-propylene glycol.

#### Summary

- 1. "Partition experiments" on the formation of cyclic acetals by the action of 1 molecular equivalent of acetylene on a mixture of one equivalent of a 1,2-glycol and one of a 1,3-glycol, indicate that the 6-membered ring forms with considerably greater ease than the 5-membered ring.
- 2. The presence of methyl groups attached to the glycol carbon atoms increases the tendency towards ring formation.
- 3. It seems probable that ethylidene glycerol, as prepared by the acetylene method from glycerol, represents a mixture of a 5- and a 6-membered cyclic acetal, the latter predominating. The product thus represents the final result of an "intramolecular partition reaction."

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

# STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. VII. THE EASE OF FORMATION AND NATURE OF CERTAIN SIX, SEVEN, AND LARGER CARBON-OXYGEN CYCLIC STRUCTURES

By Harold S. Hill and Harold Hibbert

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In the preceding communication (Part VI), the question of the relative ease of formation of certain 5- and 6-membered heterocyclic compounds was considered, and evidence submitted showing that cyclic acetals obtained from acetaldehyde and containing 6 ring atoms are formed in marked preference to those having only 5. The present investigation is an extension of this study to derivatives containing more than 6 atoms in the ring.

The importance of further experimental evidence on this subject is at once apparent from a review of the theories which have recently been advanced regarding the molecular configurations of various polysaccharides. Cellulose, for example, is regarded by Karrer² as being a polymerized form of a hypothetical anhydro cellobiose. The latter compound

¹ Antoine Chiris Co. Research Fellow.

² Karrer, Helvetica chim. Acta, 5, 187 (1922).

contains a 13-membered cyclic structure having 11 carbon and 2 oxygen ring atoms. The same investigator assigns to diamylose, and its polymer starch, a similar, 14-membered cyclic configuration. On the other hand, Irvine³ believes that the known facts regarding cellulose are best interpreted on the basis of its complex molecule being derived from an anhydrotriose unit,⁴ consisting of an 18-membered cyclic structure having 15 carbon and 3 oxygen atoms in the ring. Except for these assumptions, there exists at the present time no knowledge regarding the existence of carbonoxygen rings of this size, much less with respect to their properties and the conditions under which they are formed. In fact, examples of simple, carbon-oxygen heterocyclic structures containing even as high as 7 ring atoms are very rare, the most prominent of these being ethylidene tetramethylene glycol prepared recently by the action of acetylene on tetramethylene glycol.⁵

Before taking up the interpretation of the experimental evidence, a brief discussion is necessary of the more important factors involved in the formation of large, cyclic configurations. The problem is obviously complicated by questions such as whether an atom can rotate *freely* on the axis of a single bond, and whether there is a force which tends to keep the atom of a cyclic structure in the same plane. The great influence of these factors on the configuration of a large ring may be illustrated by the use of suitable wire models.⁶

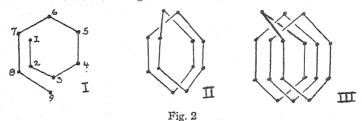
The universal existence and ease of formation of 5- and 6-membered rings would seem in itself to be strong evidence that there is a mutual attraction between all the atoms in a chain, and that it is this force which causes "cyclization." Thus in a given hypothetical case, where the assumption is made of a constant angle of valence forces of approximately 120°, a chain of 3 atoms exists in a configuration illustrated by 1–3; a chain of 4 atoms as 1–4, rather than 1–4′; one with 5 atoms 1–5 instead of 1–5′, etc., and in a 6-membered chain the systematic structure 1–6 rather than one of the large number of possible 1–6′ groupings.

- ³ Irvine, J. Chem. Soc., 123, 525 (1923).
- ⁴ It is of interest that Bertrand has recently succeeded in isolating such a triose complex.
  - ⁵ Hill and Hibbert, This Journal, 45, 3108 (1923).
- ⁶ These can be made by taking a piece of stout iron or brass wire, measuring off, for example, 3 cm., then bending this to form a given angle, say 120°; again measuring off the same distance and bending to form a second similar angle. This typifies the union of 4 atoms. By continuing, a ring may be built up of any number of atoms. It will be noticed, however, that with a larger number of atoms (7, or more) there is a considerable strain on the ring, which is the greater, the larger the number of atoms present. When this strain reaches a certain limit it is relieved by the collapsing of the simple, large ring, to give a more complex, but more stable, spiral configuration such as is indicated in II or III of Fig. 2.

Fig. 1

In other words, a mutual attraction tends to keep the atoms of a chain in one plane and at the same time prevents in some measure free rotation about a single valence linking. The absence of any directing force would allow free rotation on the axis of a single bond with the consequent displacement of the atoms from a plane so that 6' might be located at almost any point in space about 1 within the maximum length of the chain. It is believed that a systematic arrangement, 1–6, is more in harmony with our existing knowledge, than an indefinite zigzag structure⁷ represented by 1–6'. It should be noted that the relative positions of 1 and 6 would be influenced by groups attached to any of the atoms.

If the foregoing conception of the structure of an atomic chain, the atoms of which possess a constant angle of valence forces of 120°, is correct, it follows that a 7-, 8-, 9-, or higher-membered chain would exist in Form I,



the positions of 7, 8, 9, etc., being held near to 1, 2, 3, etc., respectively, by the same mutual forces which determined the configuration of the original ring. The actual forms, therefore, of closed chains containing as high as 12 and 18 ring atoms would resemble the spiral configurations indicated by II and III. In other words, cyclization in atomic chains might be expected to be a periodic function of their length, the period depending on the angles between the valence bonds, or forces, joining the atoms.⁸

⁷ This point is to be discussed by one of us (Hibbert) in a forthcoming paper dealing with the "Mechanism of Organic Reactions."

⁸ The theory would appear to derive some support from the fact that, while tetraand pentamethylene glycols readily dehydrate to give cyclic oxides, the 1-6, 1-7 and 1-8 diols do not show this property. 1-10-Decamethylene glycol, however, may be The higher periods would be less sharply defined than the first, since the greater the number of atoms in a closed chain, the less would be the strain produced by the addition or subtraction of a single atom.

The possibility of spiral ring formation was suggested by Frankland⁹ and has been emphasized by Pickard, Kenyon and co-workers,¹⁰ in their interesting researches on the dependence of rotatory power on chemical constitution. The latter show¹¹ that "in a series of normal esters of secondary alcohols exhibiting optical activity we may expect irregularities in the rotatory power... and that these irregularities are due to the fact that the ester chain of carbon atoms assumes a spiral form with about five atoms in one complete turn, entire turns being completed at the point of irregularity."

# Relative Ease of Formation of 5-, 6- and 7-Membered Cyclic Acetals

It was of primary importance to establish definitely the existence of the first period in the tendency towards ring closure. Consequently, the relative ease of formation of 5-, 6- and 7-membered cyclic acetals resulting from the action of acetylene, in the presence of a catalyst, on ethylene glycol, trimethylene glycol and tetramethylene glycol, respectively, was first investigated. It has already been shown in the last communication 12 that it is possible to apply the "partition principle" to this reaction, and that one mole of acetylene, when caused to react with a mixture of one mole of ethylene glycol, and one mole of trimethylene glycol, combines more readily with the latter, the ratio of the 6-membered cyclic structure to the 5, being approximately two to one. A similar experiment involving a partition of one mole of acetylene between one mole each of ethylene glycol and tetramethylene glycol now shows that the penta-atomic ring is formed three times as readily as the acetal containing 7 ring atoms. The existence of an optimum in the ease of ring formation with this series of compounds is therefore clearly demonstrated.

# Attempts to Prepare Cyclic Acetals Containing More than Seven Ring Atoms

The rapid decrease in the ease of ring closure in hepta-atomic configurations renders it difficult to account for the formation and stability of the much larger ring systems which are assumed to exist in the polysaccharides converted into a cyclic oxide, indicating a second period in the tendency toward cyclization. Some doubt exists as to the actual configuration of decamethylene oxide, so that the evidence is not conclusive. This product is to be investigated as well as the higher members of the glycol and polyglycol series and their cyclic acetals.

- 9 Frankland, J. Chem. Soc., 75, 368 (1899).
- Pickard, Kenyon and others, ibid., (a) 99, 45 (1911); (b) 100, 620, 1427 (1912);
   (c) 103, 1923 (1913); (d) 123, 1 (1923).
  - ¹¹ Ref. 10d, p. 7.
  - 12 This series, Part V, This Journal, 45, 3108 (1923).

except on the ground that, with sufficient lengthening of a chain, there is a recurrence of the tendency towards "cyclization." Estimating that the second "period" of ring formation in this series of cyclic acetals would occur in structures having from 11 to 13 ring atoms, an attempt was made to prepare the cyclic ethylidene derivatives of octa- and decamethylene glycols. The method used was that in which a mixture of a glycol and paracetaldehyde is heated in the presence of a trace of 40% sulfuric acid as a catalyst. Both octa- and decamethylene glycol yielded heavy, sirupy. odorless acetals which had very high and indefinite boiling points, the latter property indicating that polymerization had probably occurred. since the simpler cyclic acetals containing 5, 6, and 7 ring atoms are limpid. volatile liquids, possessing a characteristic odor. It has not yet been possible to prove definitely whether the sirups obtained from the higher glycols are cyclic structures or open-chain derivatives of indefinite size resulting from successive glycol-acetaldehyde condensations, such as  $HO-(CH_2)_9-CH_2-O-CH(CH_3)-O-CH_2-(CH_2)_9-O-CH(CH_3)-O$ -CH₂-(CH₂)₉OH, etc. Analysis for carbon and hydrogen gave values reasonably close to those calculated for the cyclic acetal, which are somewhat below the percentages of carbon and hydrogen in an open chain of the type mentioned above. In view of other possible configurations, however, it is not considered possible to differentiate by analysis alone between the cyclic and open-chain alternatives.

If our conception of large atomic rings as closed spirals (II and III) is correct, the different physical properties of the ethylidene compounds of octa- and decamethylene glycols from those of the lower homologs cannot be considered as evidence against the existence of the former in cyclic form. It is to be expected that a change of molecular structure from a simple ring to a dicyclic, closed spiral would give rise to compounds having totally different physical properties.¹³

13 In this connection it is interesting to note that in the homologous series of cyclic anhydrides of dibasic acids there is a sharply marked break in physical properties [Auger, Ann. chim. phys., [6] 22, 362 (1891). Etaix, ibid., [7] 9, 370, 387, 398, 404 (1896). Michael, J. prakt. Chem., [2] 60, 337 (1899). Voerman, Rec. trav. chim., 23, 265 (1904). Einhorn and von Diesbach, Ber., 39, 1222 (1906). Einhorn, Ann., 359, 150, 158 (1908). Staudinger and Ott, Ber., 41, 2208, 3829 (1908). Staudinger and Bereza, Ber., 41, 4462 (1908). Diels and Lalin, Ber., 41, 3429 (1908)] between succinic and glutaric anhydrides on the one hand, and adipic and the higher members on the other. The two former derivatives contain 5- and 6-membered heterocyclic configurations and closely resemble each other in their properties, being characterized by their tendency to form large crystals, and their ready solubility in solvents. Adipic anhydride differs from glutaric from a chemical standpoint only in the addition of another CH₂ group, yet this compound and the higher homologs have practically no crystalline form and are insoluble in many solvents. More important, still, is the fact that the 7- and higher-membered cyclic anhydrides exist for the most part only in a polymerized condition, while succinic and glutaric anhydrides do not polymerize. These

The suggestion is offered that "cyclization" of long chains to give closed spiral configurations is closely connected with the phenomenon of polymerization. It is difficult to explain this change in the case of polysaccharides in any other way.¹⁴ For example, Karrer's diamylose (anhydro maltose) differs from maltose itself only in that: (1) a new half-acetal type of linkage is introduced by the dehydration, and (2) a closed chain of 14 atoms has been formed. Since there are already three analogous linkages in maltose, the introduction of a fourth group of this inert type could scarcely be expected to produce any great change in properties. It is probable, therefore, that the formation of the 14-membered ring is alone responsible for the tendency of diamylose to polymerize. Furthermore, since most of the known examples of simple, cyclic structures do not polymerize, it is unlikely that merely increasing the number of ring atoms to form simple large rings would cause this property to appear. The conclusion is reached that the longer closed chains exist in the alternative, closed-spiral configurations, and that it is the greatly increased complexity of the latter which in some way (possibly an interlocking as suggested by Robinson)¹⁵ brings about polymerization.

Similar reasoning may be applied to the polymerization of the 18-membered cyclic structure of the anhydro-triose suggested by Irvine as the unit on which the cellulose complex is built up.

On the whole it appears probable that the acetal sirups obtained from the action of acetaldehyde on octa- and decamethylene glycols are polymerized forms of 11-, and 13-membered ring structures.

The present investigation was rendered difficult by the laborious processes necessary for the preparation of the higher glycols. The three which have been tried with the acetal reaction were made only in small facts would seem to indicate that the addition of a CH₂ group into the molecule of glutaric anhydride does not give rise merely to an increase in size of a simple ring, but that the 7-membered closed chain assumes an entirely different molecular configuration. A logical explanation is that simple atomic rings above a certain size become strained to a point where the structure collapses to a more stable but more complex form, the valence bonds remaining intact. This would account for the sharp change in physical properties without a corresponding break in the chemical nature of members of a homologous series.

14 The phenomenon of polymerization is one of the most important with which chemists have to deal, and at the same time, one of the least understood. It plays a leading role in animal metabolism, plant life, and industrial processes and in fact, penetrates to the roots of our very existence. It seems useless, however, to expect an understanding of the nature of the more complicated, polymerized products, such as cellulose, starch, etc., and of the factors giving rise to their formation, until the simpler cases, such as the polymerization of ethylene oxide, have been examined, and an explanation furnished. An investigation of these simpler derivatives is in progress. (Hibbert.)

¹⁵ Robinson, J. Soc. Chem. Ind., 42, 953 (1923).

amounts. It is proposed to synthesize a series of glycols, trimethylene to decamethylene, and higher if possible, as well as polyglycols, and to make a more exhaustive study of the heterocyclic structures which may be derived from them.

## Experimental Part

## Preparation of 1,4-Tetramethylene Glycol

Tetramethylene glycol was synthesized from trimethylene glycol, by first converting it into tetramethylene bromide by the method of Marvel and Tanenbaum. The reduction of the ester was the most troublesome step, but after the technical difficulties had been overcome, the method gave a yield of 60-72%. Efficient stirring appears to be of the greatest importance.

The tetramethylene bromide was converted into the diacetate by means of the procedure given by Henry¹⁷ for the similar synthesis of trimethylene diacetate. A mixture of 100 g. of tetramethylene bromide, 125 g. of potassium acetate and 225 cc. of 90% ethyl alcohol was heated for 14 hours on a steam-bath. The cooled solution was filtered from the solid potassium bromide, and the greater part of the alcohol distilled. Two layers separated, the lower of which was extracted with ether and the latter solution added to the upper layer which was then distilled under diminished pressure. After the last of the alcohol had been removed, a certain amount of potassium acetate separated. The distillation was stopped, ether added, the mixture filtered, and the ether removed. Fractionation of the solution under diminished pressure yielded 76 g. of tetramethylene acetate, b. p., 106–112°, representing a 95% yield of fairly pure material.

The diacetate was converted into tetramethylene glycol by heating with powdered potassium hydroxide¹⁷ and distilling the resulting glycol directly from the reaction mixture, under diminished pressure. The yields were poor, 34 g. of diacetate with 24 g. of potassium hydroxide giving only 9.5 g. of purified glycol, and representing a 50% yield. Calcium or barium hydroxide, in place of potassium hydroxide gave no better results.

Preparation of Ethylidene Tetramethylene Glycol.—This cyclic acetal has already been prepared from the glycol by means of acetylene and a trace of mercuric sulfate and coned. sulfuric acid.¹⁸ It may also be obtained by the following method. A mixture of 11.6 g. of tetramethylene glycol, 10 g. of paraldehyde (added from time to time) and one drop of 40% sulfuric acid was heated for 10 hours on the water-bath. The product was extracted with ether, washed with a small amount of 10% sodium carbonate solution, dried over solid potassium carbonate and fractionated. There was obtained 4 g. of ethylidene tetramethylene glycol; b. p., 125–127°; yield, 27%. There was about an equal amount of a sirup left in the flask which could not be distilled, but which was an acetal of some kind, since it was readily hydrolyzed by dilute acids into acetaldehyde and tetramethylene glycol.

Partition of Acetylene between Ethylene Glycol and 1, 4-Tetramethylene Glycol.— The procedure employed for this experiment was identical with that already described in a similar determination of the "partition value" between ethylene glycol and trimethylene glycol.¹⁹

A mixture of 18 g. of tetramethylene glycol, 12.4 g. of ethylene glycol and 4.4 liters of acetylene (the calculated amount) with 1 g. of mercuric sulfate and 1 cc. of concd. sulfuric acid as catalyst, gave 4.6 g. (b. p., 80–90°) and 2 g. (b. p., 120–130°) of the

¹⁶ Marvel and Tanenbaum, This Journal, 44, 2645 (1922).

¹⁷ Henry, Rec. trav. chim., 18, 224 (1898).

¹⁸ Ref. 12, p. 3115.

¹⁹ This series, Part VI, THIS JOURNAL, 45, 3117 (1923).

respective cyclic acetals, representing yields of 26.0% and 8.5% of the 5- and 7-membered ring derivatives, respectively. It is not claimed that these yields are more than approximations, although there is no doubt of the preponderance of the smaller cyclic ring derivative.

Preparation of Decamethylene Glycol.—Dimethyl sebacate was prepared by heating a mixture of 5 parts by weight of sebacic acid, 2 parts of methyl alcohol and 4 parts of concd. sulfuric acid for 15 hours. The product was poured into an excess of water, extracted with ether, and distilled under diminished pressure; yield of pure dimethyl ester, 90-95%; b. p., 167-168° (15 mm.).

It was found that Marvel and Tanenbaum's modification ¹⁶ of the reduction method developed by Levene and Allen ²⁰ may be applied, satisfactorily to the reduction of dibasic esters. Ninety g. of dimethyl sebacate was reduced with 138 g. of sodium, 320 cc. of toluene and 780 cc. of absolute ethyl alcohol. The yield of decamethylene glycol, m. p., 72°, was 41 g. or 60%. The procedure followed was approximately that given by Marvel and Tanenbaum for the reduction of ethyl phenoxybutyrate. ¹⁶ After the distillation of alcohol and toluene from the reaction mixture, 600 cc. of water was added and the crude solution extracted five times with ether. Evaporation of the solvent left crude decamethylene glycol which was recrystallized from a mixture of ligroin and benzene.

Preparation of Ethylidene Decamethylene Glycol, 
$$CH_3-CH_4-CH_2$$
 ??

—Eighteen g. of decamethylene glycol, 15 g. of paracetaldehyde and 4 drops of 40% sulfuric acid were heated together for 12 hours under a reflux condenser. More paracetaldehyde (10 g.) was then added to replace loss by volatilization and the heating continued for another 12 hours. The product was treated with ether, the solution washed with a small amount of 10% sodium carbonate solution and dried over solid potassium carbonate. Removal of the solvent left a viscous, colorless sirup which was fractionated under diminished pressure. The small first fraction, boiling at  $138-140^\circ$ , was found to be unchanged glycol. At  $230^\circ$  (0.5 mm.) a sirup began to distil, and the temperature rose steadily to  $320^\circ$  (0.5 mm.) at which point the distillation was stopped. The greater part of the product still remained in the flask as a colorless sirup. There had been no apparent decomposition, although the product was somewhat more viscous than at the start of the distillation. This fact, together with the rise in boiling point would seem to indicate that a polymerization of the product had been brought about by heating.

Analyses [distilled sirup, b. p.,  $230-320^{\circ}$  (0.5 mm.)]. Calc. for ethylidene decamethylene glycol,  $C_{12}H_{24}O_2$ : C, 72.00; H, 12.0. Found: C, 71.16; H, 11.8. Sirupy residue. Found: C, 71.41; H, 11.9.

Both sirups were readily hydrolyzed to acetaldehyde and decamethylene glycol by treatment with dilute acids.

Preparation of Octamethylene Glycol.—Suberic acid was obtained from castor oil by oxidizing this with nitric acid according to the method given by Markownikoff.³¹ The yield of pure acid was only about 5-6% of the weight of oil used, although earlier investigators record a higher yield.

A mixture of 115 g. of pure suberic acid (m. p., 141°) with 230 g. of methyl alcohol and 75 g. of concd. sulfuric acid was heated for six hours under a reflux condenser. The yield of dimethyl suberate, [b. p., 136-138° (14 mm.)] was 87 g., or 62%.

Dimethyl suberate was converted into octamethylene glycol by the same method

²⁰ Levene and Allen, J. Biol. Chem., 27, 435, 443 (1916); 33, 509 (1918).

²¹ Markownikoff, Ber., 26, II, 3090 (1893).

and procedure as followed in the reduction of dimethyl sebacate ester; 80 g. of dimethyl suberate, on reduction with 138 g. of sodium, 780 cc. of absolute ethyl alcohol and 320 cc. of toluene, gave 33 g. of pure octamethylene glycol; b. p., 167–168° (15 mm.); m. p., 63°; yield, 55%. Because of the greater solubility of this glycol in water, eight extractions with ether were necessary in order to remove it completely from the crude, aqueous salt solution. Prior to this extraction only the minimum amount of water necessary to dissolve part of the solid products had been added to the residue left after removal of the alcohol and toluene.

Preparation of Ethylidene Octamethylene Glycol,  $\begin{bmatrix} \mathrm{CH_3-CH} \\ \mathrm{CH_3-CH_2} \end{bmatrix}_{x}^{?}$ 

—A mixture of 19 g. of octamethylene glycol, an excess of paraldehyde (25 g.) added from time to time, and 6 drops of 40% sulfuric acid was heated for 12 hours under a reflux condenser. Extraction with ether, as in the preparation of the decamethylene derivative, yielded similar products, namely, a small amount of unchanged glycol, and a sirup having an indefinite, very high boiling point. The latter material was not analyzed, but appeared to be analogous to the sirup obtained from the reaction of acetaldehyde with decamethylene glycol, being readily hydrolyzed to the free aldehyde and glycol by means of dilute acids.

The authors desire to express their thanks to the Antoine Chiris Company, through whose generosity the work described in Parts V, VI and VII, was rendered possible. They also wish to express their gratitude to the Committee of the Warren Fund, National Academy of Sciences, for the grant made to them for the purchase of chemicals used in the course of these investigations.

### Summary

- 1. A discussion is given of ring formation and of the properties of cyclic acetals derived from high-membered glycols (1:4; 1:8; 1:10).
- 2. It is shown that the ease of formation increases from the 5- to the 6-membered rings and then diminishes again with the 7-.
- 3. It is suggested that due to the strain involved in the structures of higher-membered cyclic acetal rings, these collapse, and assume a "spiral ring formation." The tendency of atomic chains to assume the latter is probably a periodic function of the number of atoms in the chain. The properties of the individual atoms in such spiral ring formations probably vary in a "periodic manner."
- 4. The "tendency towards polymerization" and "that of long chains to undergo cyclization to give closed-spiral configurations" probably stand in intimate connection with each other.
- 5. It is considered probable that the condensation products derived from acetaldehyde and octa- and decamethylene glycol, respectively, represent polymerized cyclic acetals of the "closed-spiral type."
- 6. The possibility of the existence of starch, cellulose, etc., as polymerized, closed-spiral configurations may serve to account for the stability of such ring complexes.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL RESEARCH OF PARKE, DAVIS AND COMPANY]

#### THE AUTO-OXIDATION OF CHLOROFORM

By A. M. Clover Received October 19, 1923

Pure chloroform is known to be decomposed by the air with the formation of hydrochloric acid, phosgene and carbon dioxide.¹ The development of an oxidizing substance has also been noted and this has been referred to previously as chlorine. The literature on the subject has been brought together by Baskerville.²

As no proof exists that the oxidizing substance is chlorine, and further, as the formation of phosgene and carbon dioxide leaves no doubt that the reaction is one of oxidation, the writer was led to a study of the question, suspecting that we have here an example of peroxidation similar to that which occurs with benzaldehyde and with ethers.³

When pure4 chloroform is exposed in such a manner that it comes in contact with a sufficient supply of air, it is decomposed at a remarkable rate, a fairly good idea of which may be obtained by following the development of acidity and also of the oxidizing substance which has previously been called chlorine. A maximum rate of oxidation is obtained by filling glass-stoppered bottles to one-third of their volume and allowing them to stand in diffused light. For reasons which will become obvious later, no experiments were made in sunlight. The reaction proceeds slowly at first and the rate gradually increases from day to day. At the end of a period varying from 3 to 4 weeks the development of oxidizing substance reaches a maximum at which time the solution has frequently become hazy and green. Soon afterward nearly all of the oxidizing substance disappears. When at its maximum the solution is usually close to 0.2 N in oxidizing strength, which may be measured by its action upon acidified potassium iodide solution. During the first two weeks of the oxidation the acidity developed was about twice that of the oxidizing value. After this time the acidity showed a relative increase in value. It was measured by dissolving 1 cc. of the chloroform in 400 cc. of water and titrating with standard sodium hydroxide solution, until a permanent color was produced with phenolphthalein. Of course, this method caused the hydrolysis of phosgene or any other substance capable of hydrolysis.

- 1 Schoorl and van den Berg, Chem. Centr., 1905, II, 1623.
- ² Baskerville, J. Ind. Eng. Chem., 4, 281 (1912).
- 3 Clover, This Journal, 44, 1107 (1922).
- ⁴ All chloroform used in this work was purified by shaking the commercial product thoroughly with an equal volume of water thrice, drying it twice with calcium chloride in a filled bottle of amber glass and then distilling. A product so purified was usually free from oxidizing substance and contained only a slight trace of free acid; when this was not the case it was discarded.

Although the accumulation of oxidizing substance ceased after a few weeks, there was no decrease in the rate of decomposition of the chloroform, for the acidity continued to increase rapidly. One sample which was not exceptional became more than N in acidity in six weeks.

When the pure chloroform was saturated with water the decomposition was found to take place more rapidly, as indicated by the acidity which in one experiment became  $1.7\ N$  after an exposure of six weeks. At no time during this period was there present more than a very small amount of oxidizing substance.

It has already been observed in the case of ethers that a relatively small amount of auto-oxidation takes place in amber glass when compared with flint glass. With chloroform the rate in amber is nearly one-half that in the flint. However, the accumulation of oxidizing substance goes much further in the amber and in one experiment reached a strength of  $0.6\ N$  in about two months. At this point the strength began to fall off rapidly. Undoubtedly, light is a factor in both the formation and decomposition of the oxidizing substance.

Some experiments were carried out in an atmosphere of dry air but the results did not differ much from those previously obtained without this precaution.

# Nature of the Oxidizing Substance

After it was learned that the oxidizing substance accumulates only for a limited time and then disappears, it was possible to select solutions of considerable strength at the proper time. When such a solution was added to water the latter showed a decided test for hydrogen peroxide by means of chromic acid. By comparing the strengths of colors obtained in such experiments with those obtained with very dilute solutions of hydrogen peroxide of known strength, it was possible to learn approximately the amount of this substance obtained from the oxidized chloroform. In this way, it was determined that the amount of hydrogen peroxide which resulted from the treatment with water depended largely upon the amount of water used. When the latter was in sufficient quantity to yield a solution of about 1 part in 100,000 the yield obtained was close to 80% of the oxidizing substance contained in the chloroform. When a limited amount of water was used the yield was only a small fraction of this.

The fact noted in the preceding paragraph suggests that the hydrogen peroxide does not exist in the chloroform as such, but that it is formed by reaction with the oxidizing substance upon water. This view is confirmed by the fact that hydrogen peroxide is only very slightly soluble in chloroform. An aqueous solution of the peroxide containing about 38% of the latter was shaken thoroughly with an equal volume of chloroform. The latter was 0.008~N in active oxygen, which is only a very small

fraction of the oxidizing strength of the chloroform solutions under consideration.

Furthermore, the behavior of the oxidizing substance toward a solution of potassium iodide leaves no doubt that the hydrogen peroxide was formed through reaction with water. When the oxidized chloroform is added directly to a dilute acidified solution of potassium iodide the liberation of iodine is rapid and complete within the least time possible to make a titration. When the experiment is repeated with all factors unchanged except that the chloroform solution is first added to the water and shaken, the addition of acidified potassium iodide then results in a very slow liberation of iodine in a manner characteristic of hydrogen peroxide. The direct action of the oxidizing substance is that of a much more powerful agent, being similar to that of chlorine or hypochlorous acid.

It may be concluded that the oxidizing substance is a peroxide which is formed directly by the peroxidation of the chloroform. The fact that a good yield of hydrogen peroxide is obtained through hydrolysis only in very dilute solution makes it impracticable to isolate a considerable quantity of this substance. There is evidence of a small amount of free chlorine in the hydrolyzed product as shown by the immediate action upon potassium iodide in dilute solution. Perhaps this chlorine existed along with the peroxide in the chloroform, having been formed from it as a decomposition product. The stronger solutions of peroxide which were obtained in amber bottles always had a green color. This color disappeared on partial evaporation of the solvent as did also the characteristic action upon potassium iodide. The large loss of active oxygen which occurs when the peroxide is treated with a limited amount of water can be explained only by assuming the escape of this oxygen as gas. Chlorine is found in such a solution only to a very small extent.

It was anticipated that the peroxide could be isolated by evaporation of the unchanged chloroform. Although the strength of the peroxide solution is increased by this process, still there is much loss of peroxide and all of the latter disappears soon after removal of the solvent. The amount of residue is almost negligible. Several ether peroxides have been obtained as approximately pure residues upon evaporation of the unchanged ethers, but as the experience with chloroform is so decidedly different it seems likely that in the latter case peroxide formation does not consist in the simple addition of oxygen alone but also in the separation of hydrochloric acid as follows:  $CHCl_3 + O_2 = CO_2Cl_2 + HCI$ . It would be very difficult to prove that hydrochloric acid is formed in the primary action of peroxidation, but there can be no doubt about the presence of a monocarbon peroxide derivative which can be explained

satisfactorily only by the formula, Cl₂=C(), dichloro-carbon-peroxide.

#### Preservatives or Anticatalysts

It has been the general custom for many years to preserve chloroform by the addition of 0.5 to 1% of alcohol, and this method seems to have given perfect satisfaction so far as the development of objectionable decomposition products is concerned. It has not been shown whether the alcohol acts as an anticatalyst, preventing the oxidation of the chloroform, or whether it destroys the objectionable products by entering into reaction with them. This question has been discussed by Baskerville⁵ who has collected the literature on the subject.

In studying the action of alcohol the writer has been especially impressed by the small amount of this substance necessary to prevent the formation of even a trace of peroxide, phosgene or acid. It has been found repeatedly that pure chloroform containing 0.25% of alcohol after standing for three months in diffused light under conditions most favorable to oxidation, shows no trace of the above mentioned impurities. Starch solution was employed in testing for peroxide. The acidity was determined by the use of 0.01 N alkali. The initial acidity of the purified chloroform was usually such that 4 or 5 drops of 0.01 N sodium hydroxide were required to produce a permanent color with phenolphthalein when 1 cc. of the chloroform was dissolved in water which had been previously brought to a definite color with alkali. It will be recalled that without the addition of alcohol to the chloroform a very high acidity would have been shown by the latter at the end of six weeks. It is difficult to understand how the presence of so small an amount of alcohol could prevent, by ordinary reaction, the formation of a trace of acid. However, alcohol in sufficient quantity does destroy peroxide which has developed in pure chloroform, but a high degree of acidity remains. A sample in which the oxidation had proceeded for less than two weeks and in which the acid value was, according to previous experience, not much more than twice the oxidizing value, was treated with about 2% of alcohol. After about one-half hour the solution became turbid. In two hours practically all peroxide had disappeared but the acidity was nearly as great as it was before the alcohol was added. This experiment also confirms the conclusion previously reached, that no hydrogen peroxide is present for this would not have been destroyed.

When alcohol was used as a preservative in the proportion of 1 to 1000, a trace of peroxide was first noticeable at the end of 6 weeks when there was also found to be a small increase in the acidity of the chloroform. At 1 to 2000 the alcohol was less effective as a preservative, for the same result was obtained after about one week.

Other Preservatives.—Some other substances besides alcohol are known to have a preservative action upon chloroform. The writer se-

⁵ Baskerville, J. Ind. Eng. Chem., 4, 364 (1912).

lected for study several common organic substances of different types with the hope of throwing additional light upon the question of the role of the preservative.

Phenol, benzyl alcohol, petroleum ether, purified liquid petrolatum and methyl alcohol have been found to be very effective. Different samples of chloroform containing 1% of these substances were exposed in the usual manner for a period of five months. At no time was it possible to obtain even a slight coloration by means of potassium iodide and starch; also, not even a slight increase in the acidity could be detected in any case. It is thought that all of these substances would be perfectly effective at a greater dilution, but this has not been carefully tested except in the case of the petroleum oils.

The phenol solution was finally evaporated in a current of air. The residue was not colored and it dissolved completely in water. It was converted into 2,4,6-tribromophenol, which was found to be pure after recrystallization from dil. acetic acid; m. p., 93°.

The petrolatum solution was finally evaporated and all chloroform was removed from the residue by repeatedly adding alcohol to it and distilling off the alcohol. Finally, the residue was tested for chlorine by means of copper oxide, with negative results.

These effective preservatives represent greatly different types of substances, and it is apparent that chemical structure is not an important factor in the preserving action. As to the question of a chemical change in the preservative, the results here are in agreement with the experience with alcohol. It has not been possible to show the presence of any substance which might be expected to be formed by the oxidation or chlorination of the preservatives.

Further experiments with the petroleum oils have shown that these are considerably more effective than alcohol and this is especially significant because the former are so resistant to chemical change. Pure chloroform containing 1 part of petroleum ether in 1000 was under observation for three and a half months, during which no trace of peroxide could be detected. The same result was obtained with liquid petrolatum. At a dilution of 1 part in 2000 a trace of peroxide first appeared with liquid petrolatum after five weeks. With petroleum ether, the result was not quite so good.

Benzene, benzoic acid, ether and acetone were found to have a decided anticatalytic action but are not as effective as the substances previously mentioned. Acetic acid and carbon tetrachloride are almost without action, which proves that the preservative action is not due merely to the presence of a foreign substance.

Observations were made on the auto-oxidation of two other substances closely related to chloroform, namely, bromoform and methylene chloride.

The latter developed a decided, although very small amount of oxidizing substance after 10 weeks' standing. With bromoform the development of oxidizing substance and acid was rapid at first but it soon reached a maximum which was not large.

#### Summary

Chloroform undergoes auto-oxidation in diffused light with the formation of a peroxide, which is very probably dichloro-carbon-peroxide. This substance is formed at a gradually increasing rate and its accumulation proceeds up to a certain point, where rapid decomposition sets in. Beyond this point the oxidation of the chloroform continues, although very little peroxide is found in the solution.

The phosgene, carbon dioxide, chlorine and hydrochloric acid present in the oxidized product result from decomposition and hydrolysis of the peroxide.

The preservative plays the role of an anticatalyst.

DETROIT, MICHIGAN

#### NOTES

The Molecular Conductivity of Potassium Iodide in Epichlorohydrin.— Epichlorohydrin¹ was treated with anhydrous copper sulfate for a few days and the product distilled. It had a constant boiling point of  $115^{\circ}$ . After a second distillation the distillate was colorless and had a constant conductance of  $0.2 \times 10^{-7}$ . This could not be changed after repeated treatment and distillation. The potassium iodide used was known to have been of very high purity.

The solubility of potassium iodide in this solvent was first found by a preliminary experiment. It was found that a gram molecule in 60 liters would give just the convenient solution. Therefore, 0.0277 g. of potassium iodide was dissolved in 10 cc. of epichlorohydrin and the conductance was found by the well-known Kohlrausch method. Every necessary precaution was taken and the conductivity cell was kept in a thermostat at a constant temperature of 18.00°. The value of the cell constant at that temperature was found to be 0.260.

Mol. vol. Liters	Spec. cond. ×104 mhos	Mol. cond. Mhos
60	2.3	13.8
120	1.3	15.6
240	0.8	19.2
480	0.53	25.4

¹ A commercial product.

When the molecular conductivity is plotted against volume, a nearly straight line is obtained.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT FORMAN CHRISTIAN COLLEGE LAHORE, INDIA Received June 16, 1923

N. A. Yajnik Bodh Raj Sobti

The Points of Minimum Swelling of Ash-Free Gelatin. —In an earlier paper² we described experiments indicating two points of minimum in the curve showing the degree of swelling of gelatin as a function of Sörensen (PH) value, one at 4.7 and the other at 7.7. This finding was criticized

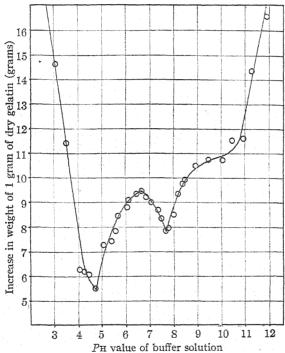


Fig. 1.—The two points of minimum swelling of ash-free gelatin.

by Sheppard and Elliott³ on the ground that the gelatin used was not ashfree. It was intimated that the point of minimum found at 7.7 was probably due to mineral impurities in the gelatin used.

- ¹ Presented before the Leather and Gelatin Division at the 66th meeting of the American Chemical Society, Milwaukee, Wis., September 12, 1923.
  - ² Wilson and Kern, This Journal, 44, 2633 (1922).
- ³ Paper presented before the 65th meeting of the American Chemical Society, New Haven, Conn., April 6, 1923.

Through the kindness of Dr. Sheppard, we secured a sample of Eastman's highly purified gelatin, which proved to be practically ash-free and gave a Sörensen value of 4.7 in distilled water. We repeated the experiments exactly as described in the earlier paper, except for using a more dilute buffer solution so as to increase the sensitivity of the measurements. In all cases, the buffer solutions had a final concentration of 0.02 M phosphoric acid plus sodium hydroxide to give the desired Sörensen value. The results obtained, at  $7^{\circ}$ , are shown in Fig. 1.

The second point of minimum, at 7.7, stands out too sharply to be attributed to experimental error and we found that the results can easily be duplicated. Moreover, Mathews and Higley⁵ studied the absorption spectrum of gelatin with changing Sörensen value and found minimum values for the wave length of maximum absorption in the ultraviolet at PH 4.68 and 7.66, coinciding with our points of minimum swelling. Since they used gelatin solutions, it was not necessary to use an extraneous buffer material. It is important to note that they used purified gelatin and regulated the Sörensen value by the simple addition of hydrochloric acid or sodium hydroxide.

That the two points of minimum have a real existence seems established, although the explanations offered as to the cause still remain in the controversial stage.

LABORATORIES OF A. F. GALLUN
AND SONS COMPANY
MILWAUKEE, WISCONSIN
Received October 8, 1923

John Arthur Wilson Erwin J. Kern

### ADDITIONS AND CORRECTIONS

1921, VOLUME 43

The Purification and Some Physical Properties of Certain Aliphatic Alcohols, by Roger F. Brunel, J. L. Crenshaw and Elise Tobin.

P. 565. In line 22, instead of "-0.00042t" read "0.0003671t"."

P. 574. Table I, under columns headed  $d_4^{25}$  and  $M_{25}^{\rm b}$ , read as follows.

n-Propyi aicon	01	<i>iso</i> -Bueyr arcone	)1
A	0.79975	A	0.79762
В	0.79952	В	0.79762
Most probable value	0.7997	C (Res.)	0.79764
$M_{25}^{\mathrm{D}}$	17.54	Most probable value	0.79763
		$M_{25}^{\mathrm{D}}$	22.22

sec-Butyl alcohol

A-III			0.80228
IV			0.80234

⁴ For method of preparation, see Sheppard, Sweet and Benedict, This Journal, 44, 1858 (1922).

⁵ Paper presented before the Leather and Gelatin Division at the 66th meeting of the American Chemical Society, Milwaukee, Wis., September 12, 1923.

0.79763

0.80224

Most probable value

0.80229

-22.14P. 575. Table II, under column headed d₄²⁵, read as follows.

n-Propyl alcohol

iso-Butyl alcohol

Authors' value

Authors' value

P. 576. sec-Butyl alcohol

0.7997

Authors' value

0.80229

P. 577. In line 7, for "k = 0.032368" read "k = 0.032368."

## 1922, VOLUME 44

Ion Activities in Homogeneous Catalysis. The Formation of Para-chloro-acetanilide from Acetylchloro-amino-benzene, by Herbert S. Harned and Harry Seltz.

P. 1478. In Equation 1, instead of "C₆H₅NClCOCH₃+ + H + Cl+" read "C₆H₅- $NCICOCH_3 + H^+ + CI^-$ ."

P. 1480. In the second line from the bottom, read "log  $F_a' = \alpha' C - \beta' C^m'$ ."

P. 1483. In the eleventh line of the text, read "whence  $E_e$  is found to be 2.14  $\times$  $10^4$  cals. between 25° and 35°, and 1.93  $\times$  10⁴ cals.," etc.

A Study of the Velocity of Hydrolysis of Ethyl Acetate, by Herbert S. Harned and Robert Pfanstiel.

P. 2201. For 
$$\frac{T'_0 - T}{T_E} = x$$
 read  $\frac{T'_0 - T_A}{T_E} = x$ .

Examination of Neoarsphenamine. II. The Constitution of the French Drugs, by A. Douglas Macallum.

P. 2581. Table II, the last three lines should read:

Element or group

Av. % found Molecular proportions

Bisulfite (-CH2OSO2Na)

29.12

1.844

Total

2.1440.278

Sulfonate (-SO₃Na)

P. 2582. Note added by author (December 18, 1922).

The general sparing solubility of these compounds in alcohols is in agreement with an arseno structure, this property having been used at one time by Bart (Ger. pat. 270,-568) to distinguish certain arseno compounds from the arsenoxides and arsines.

The Absorption of Carbon Monoxide by Cuprous Ammonium Carbonate and Formate Solutions, by Alfred T. Larson and Clark S. Teitsworth.

P. 2880. In line 26, instead of "moles per liter," read "equivalents per liter."

P. 2882. In Figs. 2 and 3, the axis of abscissa should be 4 cm. per scale division. In Fig. 2, the axis of ordinate should be 1.25 volumes per scale division.

Optically Active Dyes. I, by A. W. Ingersoll with Roger Adams.

P. 2933. In line 29, for "made up to 50 cc. in a mixture of" read "dissolved in a In line 32, for "made up to 50 cc. in a mixture of" read "dissolved in a mixmixture of." ture of."

P. 2934. In line 8, for "(70 to 75%)" read "(90 to 95%)."

P. 2935. In line 17, for "l-Ethyl(p-nitrobenzoylamino)acetic Acid" read "l-Ethyl-phenyl(p-nitrobenzoylamino) Acetate."

P. 2936. In line 4, for "d-Ethyl(p-nitrobenzoylamino)acetic Acid" read "d-Ethyl-phenyl(p-nitrobenzoylamino) Acetate."

Index of Authors. P. 2982. Omit line 7, ("McCollum, E. V., etc.").

Index of Subjects. P. 3004. Omit line reading "Nutrition, Newer Knowledge of (McCollum, book rev.).....2974.

#### 1923. Volume 45

The Action of Hydrogen Peroxide upon Certain Phenyl-Substituted Uric Acids. Fourth Paper on Purines, by F. J. Moore and Elizabeth S. Gatewood.

- P. 136. In the first line of the last paragraph after the words "shown that" insert "allantoxaidin, a close relative of."
  - P. 148. In the tenth line from the bottom of the page, for "p. 146" read "p. 140."

The Interaction of Aliphatic Alcohols and Beta-Gamma-Dibromopropyl Isothiocyanate, by Raymond M. Hann.

- P. 483, line 19, and P. 486, line 1, for "5-bromomethyl-2-ethoxy- $\Delta^4$ -thiazoline" read "5(bromomethyl)-2-ethoxy- $\Delta^2$ -thiazoline."
- P. 484, line 9, and P. 486, line 4, for "5-bromomethyl-2-hydroxyl-Δ⁴-thiazoline" read "5(bromomethyl)-2-hydroxy-Δ²-thiazoline."
- A Modification of Gillespie's Method for the Determination of Hydrogen-Ion Concentrations, by William D. Hatfield.
- P. 942. In the sub-heading of the first four columns in Table I, instead of "acid tube," "alk, tube," "acid," "alk," read "alk, tube," "acid tube," "alk," "acid,"

The System, Calcium Oxide-Carbon Dioxide, by F. Hastings Smyth and Leason H. Adams.

- P. 1167. First paragraph of article, line 10, instead of "From systems" read "From such systems."
- P. 1171. Ninth line from the bottom of the page, instead of "calcium oxide gas" read "carbon dioxide gas."
  - P. 1184. Summary, Paragraphs 2 and 4, for "1389" read "1339"."

The Use of Bromate in Volumetric Analysis. III. The Determination of Bromate in the Presence of Ferric Iron, by G. Frederick Smith.

P. 1671. Line 1. Author's added note: The sodium oxalate used in these experiments was C. A. F. Kahlbaum's best product "for analysis."

The Free Energy and Heat of Formation of Lead Monoxide, by David F. Smith and Hubert K. Woods.

P. 2637. In the third line, instead of "-0.000000257T3" read "-0.000000513T3." In the fourth line, instead of "0.000000128T3" read "+0.000000257T3."

Studies on Enzyme Action. The Relationship between the Chemical Structure of Certain Compounds and their Effect upon the Activity of Urease, by Elbert W. Rockwood and William J. Husa.

- P. 2678. In the first paragraph of the article, line 5, instead of "acids of amphoteric" read "acids or amphoteric."
- P. 2682, line 28, and p. 2688, lines 32-33, instead of "effect increasing" read "effect decreasing."

#### NEW BOOKS

Konstanten der Atomphysik (The Constants of Atomic Physics). By Dr. Walther A. Roth and Dr. Karl Scheel. Julius Springer, Linkstr. 23–24, Berlin, W. 9, 1923. 114 pp. 9 figs. 27.5 × 19.5 cm. Price \$2.00.

This is a separate printing of 32 tables (114 pp.) from the new fifth edition of "Landolt-Börnstein." As such it needs no introduction to the scientific public except to say that the same high level of thoroughness and accuracy has been maintained as in previous editions. The data purport to be complete to the end of 1921, and the many specialists who have made the selection seem to have done their work well. The German

Commission's atomic weights are used, "Avogadro's number" is called Loschmidt's, and other "scars of war" are apparent, but as a whole one feels only admiration for the achievement of such a task under the difficulties which must have beset it. The tables include among other things radioactive constants, ages of minerals, molecular magnitudes, selected wave lengths from all types of spectra, crystal structures, and many kinds of data concerning radiation. Some defective type has been used on p. 4, and at the top of Table 6, "8a," should read "6a."

NORRIS F. HALL

Fluorescenz und Phosphorescenz im Lichte der Neueren Atomtheorie (Fluorescence and Phosphorescence in the Light of the Modern Atomic Theory). By Peter Pringsheim. Second Edition, revised. Julius Springer, Berlin, 1923. viii + 228 pp. 33 figs. 22 × 14 cm.

The first edition of this excellent little monograph has been reviewed in This Journal, 44, 1602 (1922). The addition of 60 references has again brought the bibliography up to date. The text has been revised and amplified throughout to bring it into conformity with the most recent conclusions of research. Consequently a number of provisional statements in the first edition now reappear as definite and dependable conclusions. The advantages of such a revision, though it has expanded the book by only 20 pages, need not be further emphasized. It is to be hoped that the author will be able to continue this policy in later editions.

G. S. FORBES

Grundriss der Photochemie in elementarer Darstellung als Einführung in das Studium (Outline of Photochemistry, in Elementary Presentation, as Introduction to the Subject).—By Prof. Dr. J. PLOTNIKOW, Professor and Director of the Physicochemical Institute at the Royal Technical Hochschule at Agram. Walter de Gruyter and Company, Berlin and Leipzig, 1923. vi + 196 pp. 34 figs. 23 × 15 cm. Price \$1.00.

The misfortunes of the author between 1917 and 1920 due to political and economic convulsions in Russia and surrounding countries have been recounted in a review of "Allgemeine Photochemie," This Journal, 43, 2260 (1921). Later he received news that "the exponents of the new civilization" in Russia had converted into cigarette wrappers the manuscript of his "Photochemisches Praktikum" which, ready for the press, had been stored in Moscow. Accepting a call to Agram with high hopes of resuming experimental research, he found the laboratory appropriated for other purposes. His inextinguishable creative impulse then found expression in the present work, which he describes as a summary of his previous books, but in elementary form, intelligible to all desiring to follow the newer developments of natural science.

The beginnings of photochemistry among the ancients and its progress down to recent times interest the author more than the theorizing of the last ten years. The Bohr atom and Einstein's photo-equivalence are indeed more adequately treated than in "Allgemeine Photochemie." The author, however, frankly distrusts these as a foundation for photochemical theory. The complete omission of various hypotheses and theories which have recently been the subject of much discussion may have seemed necessary in view of the permissible size of the book and in view of the audience for which it is intended. Plotnikow's own well-known convictions regarding photochemical valence, kinetics, and temperature coefficients are developed at some length. The present divergence of opinion with regard to such matters might have been more distinctly stated. Examples and applications of photochemical action are given in quantity and variety sufficient to whet the reader's appetite for wider information along these lines. Considering the author's thorough knowledge of photochemical technique and his important contributions towards its improvement, an exposition in greater detail would have been welcome.

The author brought to his task the resources of a lifetime of experimental research, technical experience and deductive thought in this domain of science. He has triumphed over crushing anxieties and disappointments, and has produced a highly readable and instructive book which meets a real need in chemical pedagogy. For him, moreover, photochemistry is a passion as well as a problem, and his enthusiasm must infect the most casual reader.

G. S. Forbes

The Determination of Hydrogen Ions. An elementary treatise on the hydrogen electrode, indicator and supplementary methods with an indexed bibliography on applications. By W. Mansfield Clark, Ph.D., Professor of Chemistry, Hygienic Laboratory, United States Public Health Service. Williams and Wilkins Company, Baltimore, U. S. A. Second edition, reprinted, June, 1923. 480 pp. 42 figs. 23.5 × 15.5 cm. Price net, postpaid, \$5.00, United States, Canada, Mexico, Cuba; \$5.50, other countries.

This second edition gives a detailed exposition of "the two methods which are in use daily by workers in several distinct branches of biological science." Colorimetric methods and the electrometric method for measuring hydrogen-ion concentrations and various forms of apparatus are described fully. Sufficient theory is presented to give the experimenter a good understanding of the meaning of his results. Supplementary methods are also briefly reviewed, with references, and an extensive bibliography on methods and applications of hydrogen-ion determinations is given.

Some of the chapters of the first edition have been rewritten and all have been brought up to date, resulting in a work of 480 pages as compared with 312 pages in the original issue. A number of additions are worthy of special mention. A long list of indicators with their colors and ranges of usefulness has been added. The chapter on approximate indicator

methods has been greatly expanded. An elementary description of the potentiometric method for measuring electromotive forces has been added to the description of the electrometric method with more or less repetition in a later chapter. However, according to the footnote on p. 149, this matter needs emphasis. Descriptions of the ballistic galvanometer and electrontube methods of measuring electromotive forces have been added. The chapter on reduction potentials has been considerably extended and interesting relationships between the hydrogen electrode, metal electrodes in solutions of metal ions, and oxidation-reduction electrodes are pointed out. A description of the quinhydrone method brings the chapter on supplementary methods up to date. Over 900 references have been added to the bibliography, making a total of more than 2,000 references on hydrogen-ion methods and their applications in various branches of science.

In the chapter on standardization of measurements of Sörensen values  $(P\mathrm{H})$  the author points out that the electrometric method measures only ratios between concentrations, so that for the calculation of  $P\mathrm{H}$  values a determination of one concentration by an independent method is required. Sörensen assumed that conductance data gave the correct degree of dissociation for 0.1~M hydrochloric acid solution and based his  $P\mathrm{H}$  values on that. Recent work on activities has shown that Sörensen's assumption was undoubtedly in error, but in the meantime a vast amount of hydrogen-ion data has been accumulated in which Sörensen's value for the 0.1~N calomel electrode has been accepted. In view of the still unsettled state of the newer conceptions of electrolytic dissociation and the possibility of further changes, and also in view of the large amount of data based on Sörensen's value for the calomel electrode, the author wisely recommends that Sörensen's value continue to be used for the present.

A few minor points where improvement could be made seemed worthy of mention. Some of the tables lack titles, notably Table 3. The first paragraph in small type on p. 44 seems out of place. The sections on the theory of concentration cells, pp. 144 and 154, should contain some mention of the liquid-junction potential difference, which is neglected in the treatment. The statement that no important chain can be constructed without involving liquid-junction potentials (p. 163) is too general.

This is a complete and useful book and should be in the hands of all who work on hydrogen-ion concentrations. That it fills a need is evidenced by the exhaustion of the reprint of the first edition and the second edition.

WARREN C. VOSBURGH AND MARION EPPLEY

Oxidations and Reductions in the Animal Body. By H. D. Dakin. Second edition. Longmans, Green and Co. New York, London, Toronto, Bombay, Calcutta and Madras, 1922. ix + 176 pp. 24 × 16 cm. Price \$2.00 net.

Ten years have elapsed since the first edition of this Monograph appeared. For the most part, the addition of new experimental data and oc-

casional alterations in opinion are all that has been attempted in revising it, but the chapter on The Carbohydrates—the one most affected by progress made in the ten-year period—has been to a large extent recast. It is of interest that the new matter of this chapter deals chiefly with the earlier steps in the cleavage of glucose, before oxidation has become involved at all, for this seems to show that Dakin has already begun a task which, in his preface, he sets himself for the future. There he says: "It has become increasingly clear in recent years that the oxidations and reductions occurring in the living body are so closely interwoven with other types of reaction, especially condensation and hydrolysis, that it would seem that their consideration apart from other metabolic changes was becoming unduly artificial and could not be justified much longer." A section on the formation of sugar from fatty acids, and a few others not to be found in the original edition, also bear witness to the same tendency.

In the beginning, the author undertook to treat his subject almost wholly from the standpoint of the fate of organic compounds in the animal body, and little attention was paid to the mechanism of their oxidation or reduction. The space devoted to this question has now been about doubled; Wieland's dehydrogenation theory receives particular attention, and this and other developments relating to the participation of water in oxidation-reduction processes lead finally to an account of the remarkable catalyst (glutathione) recently discovered by Hopkins in animal and plant tissues.

The book will continue to be a mine of ready information to those interested in this field. It is to be hoped that the author can now find time to revise it at more frequent intervals, for no other publication covers the same ground.

CYRUS H. FISKE

Chemie der Pflanzenzelle (The Chemistry of the Plant Cell). By Dr. Viktor Grafe, Professor of the Biochemistry of Plants at the University of Vienna. Gebrüder Borntraeger, Berlin, 1922. viii + 420 pp. 32 figs. 25.5 × 16.5 cm.

In this book the physiology of plants is treated from the point of view of the energy transformation involved, with the structural and chemical aspects of the subject as a background. There are three portions, the first of which includes a descriptive treatment of such fundamental physicochemical processes as osmotic pressure, interfacial tension, and colloidal behavior; the second section treats of the structure of plants and the chemistry of their components, including enzymes, pigments and toxins; and the third and largest section deals with the dynamic chemistry of plants, particularly as displayed in the processes of photosynthesis and the perception of and response to stimulus.

The first section is the least satisfactory: the explanations are often cumbersome and the examples poorly chosen; it is often difficult to under-

stand the author's meaning. The chapters on stimulation and response show the author at his best.

The book as a whole is poorly organized, and reflects by its errors of citation and its neglect of recent important researches the author's lack of foreign periodicals. The author displays a not unusual fault in being hypercritical of theories which cannot conveniently be reconciled with those which he himself supports.

All life processes are considered first of all as transformations of energy; every theory to be acceptable to the author must account satisfactorily for the intake, storage or release, and outgo of energy. This alone makes the book unusually suggestive; the treatment of photosynthesis, and of stimulus and response is well worth a thoughtful perusal, even though the reader may remain unconvinced or even at times doubtful of the real meaning. Another striking feature of the book is the constant invocation of vaguely defined surface phenomena as explanations of vital phenomena.

The author does not successfully generalize his conclusions; in fact, he seems to despair of the ultimate solution of many problems. The book will appeal to those who insist upon meticulous observance of detail; those who ruthlessly demand clear and concise generalizations will hardly be satisfied.

S. C. Brooks

Practical Bacteriology for Chemical Students. By David Ellis, Ph.D., D.Sc., Head of the Department of Bacteriology and Botany in the Royal Technical College, Glasgow. Longmans, Green and Company, 55 Fifth Avenue, New York; 39 Paternoster Row, London, E. C. 4; Toronto, Bombay, Calcutta and Madras, 1923. viii + 136 pp. 55 figs. 19.5 × 13 cm. Price \$1.50.

David Ellis, the author, is already known to American workers in the field of bacteriology through the medium of his textbook, "The Outlines of Bacteriology," and a later work, "The Iron Bacteria." He has also contributed numerous monographs on the subject of the iron bacteria which have special interest for the waterworks biologist and engineer. In all of these he has shown an ability to present fundamental information in an effective way.

His reason for compiling the little volume which is here reviewed is that "in the study of Chemistry there are many avenues of research which are closed to the intending investigator owing to a lack of knowledge of the elementary principles of bacteriology." If the book is an aid to overcoming this deficiency, it is a real contribution to scientific literature. It is the judgment of the reviewer that the book does this and that it will appeal most strongly to the class it seeks to reach.

There are twelve chapters of about equal length, each of which takes the form of a series of laboratory exercises designed to acquaint the beginner with fundamental principles and procedures in bacteriology and to familiarize him with the working tools of the science. Discussion of the subject matter of chapters and explanation of results are interspersed with the exercises. The latter are clearly set apart, each step is numerically indicated, formulas are given for solutions and examples presented for the calculation of results. There are 55 figures, most of which are conventionalized drawings designed to set forth essential details. The book is a manual of elementary procedures amplified by the minimum of discussion and designed to serve as a guide to the acquisition of more complete knowledge.

The first eight chapters deal with such subjects as bacteriological apparatus, culture media and their use, staining, morphological and physiological characteristics of bacteria, biochemical activities and methods of isolation and numerical estimation. The ninth and tenth chapters deal with the examination of water and sewage. Usual procedures are given and also confirmatory tests for *Bact. coli communis*. The latter do not include some of the more recent tests which have largely supplanted, at least in this country, the older tests and which give a far better idea of the fecal or non-fecal origin of colon forms. Methods for the identification of *Bact. enteritidis sporogenes* are also given in detail. The two concluding chapters deal with yeasts and moulds. The novitiate in the science will find a great deal in these chapters which will acquaint him with the principal types of these organisms, methods for their culture and their biochemical reactions.

There are certain omissions in information which, if added, would not greatly increase the size of the book and would add considerably to its value.

A short description of the microscope would be of great value to many students of chemistry. The writer has found that a great number of such students are entirely unfamiliar with this delicate instrument which is so invaluable in many branches of science. The different morphological groups of bacteria could well have been described to acquaint the new student with the exterior appearance of these cells as seen under the microscope.

No mention is made of the adjustment of culture media reaction by means of hydrogen-ion determinations, nor of the use of hydrogen-ion concentration in determinations of acidity of cultures. This practice has almost displaced former titration methods, which deserve mention only as secondary procedures.

The book as a whole merits approval from the standpoint of what it purports to be. Many of the exercises will provide teachers as well as students with suggestions for laboratory work.

Rhus Dermatitis from Rhus Toxicodendron, Radicans and Diversiloba (Poison Ivy). Its Pathology and Chemotherapy. By James B. McNair. University of Chicago Press, Chicago, Illinois, 1923, xi + 298 pp. 18 figs.  $23.5 \times 5$  cm. Price \$4.15 postpaid

With the exception of Chapter XII, the remaining fifteen chapters of this book represent a collection of reprints of papers previously published by the author in various botanical and medical journals. The guiding aim is to establish a scientific basis for the treatment of dermatitis produced by the poisonous constituents of the rhus species (poison ivy, poison oak, etc.). It is stated in the preface that "The investigation of this poison has been carried on from the standpoint of pharmacology, of botany and of chemistry." The botanical and pharmacognostic features are considered in the first eight chapters, which abound in historical reviews and summaries of the literature. The original work along botanical lines is found in these chapters and appears to be sound. Probably the best part of the book is in Chapter X, which deals with the "Chemistry of the Poisonous Principle." This is claimed to be a polyhydric phenol, named by the author "lobinol" (from Rhus diversiloba or poison oak). It is not a definite chemical substance, but appears to be a vellowish-brown, viscous (oily?) residue (p. 93, analytical scheme) with phenolic properties, and neither a protein nor a glucoside. It may be a mixture, similar to or identical with toxicodendrol, the oily constituent of Rhus toxicodendron (poison ivy), first described by Pfaff. Hence, the reader is left in doubt as to the real identity of the constituent, and as to the justification of coining a new name ("lobinol") for it.

Chapter XIV deals with immunity to the poison and consists almost entirely of a review of the literature. The author argues against the production of immunity by the administration of the poison, but is of the opinion that natural immunity exists against it, though this is usually relative and seldom absolute.

Coming to Chapters XV and XVI, which deal with remedies for and treatment of the dermatitis, disclosure of the rational remedy would be expected, for the author states in the preface "Botany and pathology combined with a chemical knowledge of the structure of the poison have yielded a rational remedy for Rhus dermatitis." However, this is not the case, and for the following reasons: (1) The structure and nature of the poison remain unsolved. (2) Erroneous speculations in pharmacology cannot furnish the basis of a rational treatment. For instance, it is stated on pp. 113–114 that "The erythrocytes contribute hemoglobin the iron of which has the power to combine with lobinol. Likewise the blood brings glucose which on its conversion into glucuronic acid, probably has power to combine with the noxious properties of lobinol." Similar ideas are reiterated on p. 176. Moreover, if it is true that "There is reason to

believe that Rhus poison is not transmitted by body fluids....." (p. 114), these speculations could have been omitted. (3) Out of a long list of therapeutic agents and trials, the most suitable remedy settled upon by the author is a lotion containing ferric chloride. This is not new. Metallic salts (lead acetate, etc.) are well known to be effective precipitants of the poison and useful in treatment of the dermatitis. (4) The remaining measures and adjuncts in the treatment proposed by the author are familiar and largely empirical, inclusive of the paraffin treatment, which had been exploited during the World War for severe skin burns from flame projectors, etc.

From what is known of skin irritants ("dermitant," used by the author presumably means the same) in general, including war compounds, etc., the designation of rhus dermatitis as a "specific disease" is not justified. The use of the heading, "Chemotherapy....," for the various and mixed treatments outlined in Chapter XVI is not in accordance with the accepted meaning of the term.

On the whole, this book will furnish interesting and profitable reading for the general reader. However, for the physician and investigator the inclusion of considerable irrelevant and redundant material reduces its usefulness. This exists on pp. 109, 110, 122, 132, 138, 142, 144, 146, in most of Chapter XV which contains a six-page list of remedies, most of which are obsolete, and among the 34 pages of "abstracts," really detailed descriptions, of clinical case histories in the Appendix. In the Appendix there are 77 pages of a systematized bibliography pertaining to rhus and other matters, a good part of which will be useful to future students of the subject. In view of the great difficulties of investigating skin irritants and the practical nature of the problem of rhus dermatitis, the efforts and aim of the author are laudable. However, it may be doubted if our knowledge of rhus dermatitis has been advanced since the work of Pfaff in 1897.

P. J. HANZLIK

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## **PROCEEDINGS**

OF THE

# American Chemical Society

FOR THE YEAR 1923

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## Proceedings

#### DIRECTORS' MINUTES

The Directors of the American Chemical Society met at the Chemists' Club, New York City, at 3 P.M., Friday, November 24th, with President Edgar F. Smith in the chair and the following Directors present: W. D. Bancroft, A. D. Little, H. P. Talbot, John E. Teeple, M. C. Whitaker and Charles L. Parsons.

It was voted that the Secretary should continue his present policy of sending the final programs of meetings only to members in the immediate vicinity of the meeting, to corporation members, to the Councilors, to the chairmen and secretaries of local sections, and to those who make written request therefore of the secretary previous to the meeting.

The Secretary was authorized to issue a charter for a local section to be formed at Akron, Ohio, covering territory immediately contiguous thereto, such as Summit County, as soon as the properly signed petition and waiver of jurisdiction is received therefor.

It was voted to authorize the Treasurer to make loans and pledge the collateral of the Society therefor to an amount not exceeding Forty Thousand Dollars annually when in his judgment it is necessary to do so to meet the necessary current expenditures of the Society.

The Treasurer reported that he had borrowed \$25,000 at the Farmers Loan & Trust Co. on Nov. 9, 1922 to meet current expenses.

It was voted that the Editor of the Journal of Industrial and Engineering Chemistry be authorized to re-lease for one year the premises now occupied by him.

It was voted that special reprints, such as theses, be handled through the same channels as the regular reprints and billed from the Secretary's office.

It was moved that in the budget voted to the various editors they be limited not simply to the funds allotted, but also to the number of pages indicated.

It was voted to authorize the Editor of the Journal of Industrial and Engineering Chemistry and the Director of the News Service to issue a twelve-page news edition of that Journal to be separately paginated and to be published on the 10th and 20th of each month.

On recommendation of the Committee to Consider the Question of a non-Society Employment Bureau, and in furtherance of the vote of the Council favoring a clearing house for employment information, as printed on page 96 of the Proceedings for 1922, it was further voted that such part of four pages of each issue of the News Edition as might be needed should be used to furnish such information. The Directors added \$2100 to the budget to cover this service and deducted the cost of printing the advertising pages now devoted to "classified advertisements." The Directors understood that these pages would be used for announcements of positions open and situations wanted by members of the Society. In general, these announcements are to be supplied by the employment committees of local sections and from educational institutions. Under proper limits to be formulated, the pages will also be open to any paid member of the Society seeking employment. It shall, however, be definitely printed in each issue that the Society assumes no obligation as to the qualifications of employees or responsibility of employers.

The following budget was then unanimously adopted for 1923:

#### ESTIMATED INCOME

	Budget	Budget
	1922	1923
Dues	\$175,000.00	\$175,000.00
Subscriptions	21,000.00	22,000.00
Back Numbers	5,000.00	5,000.00
Reprints	1,800.00	2,500.00
Postage	4,000.00	4,000.00
Advertising	86,250.00	94,500.00
Interest	6,000.00	5,400.00
	0,000.00	0,100.00
Total	\$299,050.00	\$308,400.00
EXPENDITURES		
	Budget	Budget
	1922*(a)	1923
Journal American Chemical Society:		
Editor's Salary	\$ 1,500.00	\$ 1,500.00
Editorial Assistance	900.00	750.00
Clerical and Office Expense	2,200.00	2,450.00
Printing (2700 pp. 1922) Maximum		
3300 pp. 1923	40,500.00	42,300.00
	\$ 45,100.00	\$ 47,000.00
	Ψ 10,100.00	φ 11,000.00
Chemical Abstracts:		
Editor's Salary	\$ 4,500.00	5,000.00
Associate Editor's Salary	2,750.00	3,000.00
Second Assistant Editor's Salary	1,800.00	2,000.00
Abstractors	10,000.00	9,700.00
Clerical	5,800.00	6,000.00
Office Expenses. Printing (4763 pp. 1922) Maximum	1,000.00	1,300.00
5300 pp. 1923	65,700.00	65,100.00
Formula Index		2,900.00
		manuscriptor and control of the
	\$ 91,550.00	\$ 95,000.00
	\$ 02,000.00	φ σομοσοίος
Journal of Ind. & Eng. Chemistry:		
Editor's Salary	\$ 10,000.00	\$ 10,000.00
Associate Editor.	3,600.00	3,300.00
Assistant to Editor.	2,800.00	2,900.00
Clerical		
Staff Correspondents	6,900.00	7,870.00
	2,700.00	2,920.00
Office Expense.	1,800.00	1,724.00
Rent	2,058.00	1,766.00
Traveling Expense	2,000.00	1,900.00
Printing (1080 pp. 1922) Maximum		
1320 pp. 1923	39,342.00	41,620.00
	\$ 71,200.00	\$ 74,000.00

	Budget 1922	Budget 1923
News Service:*(b)		
Technical Manager	\$ 5,000.00	\$ 5,000.00
Office Assistants	1,200.00	1,820.00
General Expenses	3,790.00	2,600.00
Traveling Expenses	1,000.00	1,000.00
Rent	532.00	720.00
News Edition Industrial & Engineering Chemistry		7,000.00
	\$ 11,522.00	\$ 18,140.00
Employment Information: *(c)	• • • • • • • •	2,100.00
Secretary's Office:		
Secretary's Salary	\$ 5,000.00	\$ 5,000.00
Clerical	10,500.00	10,700.00
Expenses	4,000 00	4,200.00
Rent	1,800.00	1,800.00
₩	\$ 21,300.00	\$ 21,700.00
Treasurer's Office:		
Treasurer's Salary	\$ 1,000.00	\$ 1,000.00
Clerical	1,500.00	1,500.00
Expenses		600.00
Audit 1922	800.00	400.00
	\$ 3,300.00	\$ 3,500.00
President's Office:		
Travelling Expenses	\$ 1,000.00	\$ 1,000.00
Office Expenses	200.00	200.00
	\$ 1,200.00	\$ 1,200.00
Scientific Monographs:		
Salary	\$ 1,000.00	\$ 1,000.00
Expenses	60.00	60.00
	\$ 1,060.00	\$ 1,060.00
Technological Monographs:*(d)		
Salary	\$ 1,000.00	
Expenses	25.00	
	\$ 1,025.00	
Advertising:		
Printing Advertisements	\$ 38,243.00	\$ 33,000.00
BACK NUMBERS	2,000.00	1,500.00
Local Sections	8,500.00	8,500.00
Incidentals	1,500.00	2,000.00
General Meetings	2,000.00	2,000.00
Tables Physical Constants	500.00	500.00
Metric System Committee	100.00	
Grand Total	\$300,100.00	\$311,200.00

- *(a) The 1922 budget as printed was on a 10% reduction of printed pages for each journal from the amount requested by the editors. This 10% was restored some three months later, so that the 1922 budget in the case of each journal is less than actual expenditures. Also, approximately \$3200 spent for Formula Index for 1922.
- *(b) The extra cost of the News Service Edition of *Industrial and Engineering Chemistry* will be largely paid for by extra advertising in 1923 and is expected ultimately to be a source of actual revenue.
- *(c) The committee of the Council originally recommended \$5,000 for this item, but changed it to \$2,100 in view of the facilities offered by the News Edition.
- *(d) Expenses of Technological Monographs in 1923 are carried in the *Industrial* and Engineering Chemistry budget.

Charles L. Parsons, Secretary

#### COUNCIL

The following communication was sent to the Council on November 25th:

#### AMERICAN CHEMICAL SOCIETY

November 25, 1922

Council of the American Chemical Society:

Gentlemen: The following members have been duly nominated for the offices indicated for the years 1923 and 1923-1925. Kindly check your choice with an X and return the ballot on or before December 16th.

Kindly note that by vote of the Council the names are arranged in alphabetical order and not in the order of the nominating vote.

Very truly yours,

CHARLES L. PARSONS, Secretary

President.—1923 only (one to be chosen) (alphabetically arranged): E. C. Franklin, James F. Norris, S. W. Parr, Charles L. Reese.

Directors.—1923-1925, inclusive (two to be chosen) (alphabetically arranged): Wilder D. Bancroft, William Hoskins, John Johnston, S. W. Parr.

Councilors-at-Large.—1923-1925, inclusive (four to be chosen. Ballot is void unless four are voted for) (alphabetically arranged): Roger Adams, C. A. Browne, H. N. Holmes, G. N. Lewis, Ralph H. McKee, Wm. McPherson, C. S. Miner, S. W. Parr.

The returns of this ballot were counted on the evening of December 16th by a committee consisting of L. I. Shaw, H. E. Howe and Charles L. Parsons, and the following officers were elected:

President: E. C. Franklin.

Directors: Wilder D. Bancroft, William Hoskins.

Councilors-at-Large: Roger Adams, G. N. Lewis, Ralph H. McKee, Wm. Mc-Pherson.

Charles L. Parsons, Secretary

#### MEMBERS ELECTED BETWEEN NOVEMBER 15 AND DECEMBER 15, 1922

Addicks, Allen, 106 S. 36th St., Philadelphia, Pa. Adler, M., 105 E. Healy, Champaign, Ill. Albert, Raymond J., 1140 South High St., Columbus, Ohio. Alfend, Samuel, 1909 Biddle St., St. Louis, Mo. Anderson, C. Ivar, 208 South Matthews St., Urbana, Ill. Anderson, J. Arthur, 64 E. College St., Oberlin, Ohio.

Anderson, William Theodore, Jr., Graduate College, Princeton, N. J.

Austin, Dr. R. S., Cincinnati General Hospital, Cincinnati, Ohio.

Ayers, Lorenz K., 4425 McPherson Ave., St. Louis, Mo. Azami, Kosuke, Laboratory of Applied Chemistry, Imperial Univ. Kyoto, Japan. Beaver, Jacob Julius, Havemeyer Hall, Columbia University New York, N.Y. Becherer, Robert Charles, 359 Vine St., W. Lafayette, Indiana. Berman, William, 431 W. Division St., Chicago, Ill. Bernstein, Joshua, 3936 Gladys Ave., Chicago, Ill. Blakeney, Clifford, 144 Englewood Ave., Buffalo, N. Y. Bloxsom, Allan, 4402 Travis St., Houston, Texas. Boss, A. Evan, 337 Broadway, West, Vancouver, B. C., Canada. Boynton, Henry S., 25 Oak St., Orono, Maine. Bradt, Wilber, 537 So. Lincoln St., Bloomington, Indiana. Braden, Ralph H., 55 Plymouth Ave., Rochester, N. Y. Bricka, H. V., 2525 O St., Lincoln, Neb. Brogniez, Frank P., Rice Institute, Houston, Texas. Brooks, Arthur M., Y. M. C. A., 40 Lawrence St., Lawrence, Mass. Bubb, John Carroll, 719 9th St., N. E., Washingotn, D. C. Byron, Milton L., 113 Oak Ave., Ithaca, N. Y. Calvery, H. O., 209 John St., Champaign, Ill. Camp, H. W., Empire Refinery, Box 2067, Tulsa, Okla. Caplan, Solomon, 725 Home St., New York City. Cappuyns, Alphonse, 139 rue Victor Beauduin, Tirlemont Belgium. Carey, James, S., 1934 N. Second St., Harrisburg, Pa. Carlin, Thomas J., 68 Pearl St., Bangor, Maine. Chalmers, James A., Phi Eta Kappa House, Orono, Maine. Clark, James Maitland, Judd Hall Wesleyan University, Middletown, Conn. Claude, George, Ste. Chimique, Grande-Paroiste, Moutereau, Seine et Maine, France, Cohen, Frank L., 1006 S. Fifth St., Champaign, Ill. Cook, John S., Rice Institute, Houston, Texas. Cook, Roy S., 900 West Main St., Charlottesville, Va. Crockford, H. D., Box 935, Chapel Hill, N. Car. Crane, George D., 3305 South Michigan Ave., Chicago, Ill. Daude, E. F. B., Owyhee Hotel, Boise, Idaho. Diller, Carroll, 1302 Q St., Lincoln, Neb. Doehring, Carl F., 2302 Louisiana St., Houston, Texas. Dougherty, Edward T., Box 746 Falls Station, Niagara Falls, N. Y. Downs, Fred Caden, 3817 Vernon Ave., Chicago, Ill. Drew, Raymond L., 4624 Larchwood Ave., Philadelphia, Pa. Drew, Thomas B., R 406, Tech. Dorms, Cambridge, 39, Mass. Dufour, Robert E., 328 S. Harvey Ave., Oak Park, Ill. Dunham, Alice, 6051 Ellis Ave., Chicago, Ill. Durham, Edward J., Reed College, Portland, Oregon. Dyer, Colver P., 11 Grove St., Winchester, Mass. Eastman, Gertrude T., Winthrop College, Rock Hill, S. Car. Erickson, J. L. E., Rice Institute, Houston, Texas.

Efficason, J. L. H., Rice Institute, Houston, Texas

Finkle, Philip, Hotel Whitecotton, Berkeley, Cal.

Fischer, Herbert G. M., 129 Ferris Place, Westfield, N. J.

Fogler, M. F., 174 Chem. Bldg., Urbana, Ill.

Foster, Robert H. K., 1241 Cambridge Ave., Columbus, Ohio.

Fox, Kent R., 34 Noyes, Portland, Maine.

Freeman, Louis Bryant, 73 Fayette St., Cambridge, Mass.

Gamble, James L., 33 Edge Hill Road, Brookline, Mass.

Gapinski, John, 1518 Elk Grove Ave., Chicago, Ill.

Gault, Edwin Sartain, Sacred Heart Hospital, Allentown, Pa.

Geddis, Clarence R., 229 Faneuil St., Brighton, Mass.

Gilkey, Wm. K., 2402 N. Main St., Dayton, Ohio.

Gillman, Jos. L., Jr., Rice Institute, Residential Halls, Houston, Tex.

Given, Jacqueline, 1029 9th St., Boulder, Col.

Gnagey, F. Emerson, Chestnut St., Ashland, Ohio.

Goodwin, Harry M., Mass. Inst. of Tech., Cambridge, Mass.

Gordon, Lynn S., 331 East Jefferson St., Ann Arbor, Mich.

Gray, A. E., 910 S. 3rd St., Champaign, Ill.

Green, Rose Mary ,903 W. Springfield Ave., Urbana, Ill.

Greenbaum, Frederick, c/o Mr. Dienstag, 134 W. 111th St., New York City.

Gudkov, V. F., Mysore Distillat and Iron Works, Bhadravati, India.

Gunderson, Lewis O., 710 South Main St., Bloomington, Ill.

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Gupta, Sailendra Nath, 1896 Sutter St., San Francisco, Cal.
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Hall, Donald Douglass, 1662 Hower Ave., East Cleveland, Ohio.

Healy, G. E., Amalgamated Sugar Co., Burley, Idaho.

Heister, Louis, S. E. Cor. 7th and Elm, Cincinnati, Ohio.

Helmer, Oscar M., 404 35th St., Champaign, Ill.

Hiki, Osamu, Nakachoja-machi-Shimmachi, Kyoto, Japan.

Hill, Allan, 3131 Michigan Ave., Chicago, Ill.

Hoar, Gerald J., 115 Van Buren St., Joliet, Ill.

Holroyd, G. W. F., Technical College, Blackburn, Lancashire, England.

Hooper, Henry S., 53 Veazie St., Old Town, Maine.

Hughes, Edward W., 702 E. Buffalo St., Ithaca, N. Y.

Hunneman, Roger D., 20 Prescott St., Cambridge, Mass.

Hunter, J. E., 8 College Ave., Columbia, Mo.

Jenne, Lyle L., Philadelphia Bureau of Water City Hall, Philadelphia, Pa.

Joachim, Benjamin, 745 E. 175th St., Bronx, New York City.

Johnston, Frederick A., Prince Bay, N. Y.

Kadowaki, Kiemon, c/o Mrs. Yatsugi Yoshie, Shinkarasumaru-Kaminokiridoshi agaru-higasi, Kyoto, Japan.

Kalichevsky, Vladimir, 750 East Green St., Pasadena, Cal.

Katti, M. C. T., University Station, Urbana, Ill.

Kaufmann, Wilford Edward, 408 W. Main St., Urbana, Ill.

Kelley, Elmer A., 1437 W. 6th St., Riverside, Cal.

Kelly, Stephen E., 622 Henry St., Alton, Ill.

Kirkwood, John G., 3901 East Second St., Wichita, Kans.

Kitchen, John C., Jr., 801 Broadway, Bethlehem, Pa.

Knipscher, John E., Rockhurst College 52nd & Troost Ave., Kansas City, Mo.

Kolouch, Joseph Frederick, 180 Main St., Orono, Maine.

Kramer, Martha M., Kansas State Agricultural College, Manhattan, Kans.

Ladd, E. V., 2085 Marlowe Ave., Lakewood, Ohio.

Lambert, L. B., 361 Torrence Ave., Hammond, Indiana.

Lawry, Otis C., 100 Main St., Fairfield, Maine.

Laymon, Howard W., Mead Pulp & Paper Co., Chillicothe, Ohio.

Lindeman, Theo. W., 3420 Michigan Ave., Chicago, Ill.

Lindsay, James D., 913 E. Huron St., Ann Arbor, Mich.

Lord, Edward T. W., 316 W. Packer Ave., Bethlehem, Pa.

Lubin, C. I., B-10 Landon Ct., Cincinnati, Ohio.

Lucasse, Walter W., 260 So. 38th, Philadelphia, Pa.

MacCorquodale, Donald W., Illini Hall, Champaign, Ill.

Malvea, B. B., Ewing Christian College, Allahabad, India.

Marz, Meyer H., 23 Branch St., St. Louis, Mo.

May, Arthur J., 24 Camp St., Newark, N. J.

McDonald, Henry, Jr., 343 Washington St., Middletown, Conn.

McKenzie, Bernard F., Mayo Foundation, Rochester, Minnesota.

Miller, Herbert J., 802 Ellicott St., Buffalo, N. Y.

Molnar, Steven, 3409 West 60th St., Cleveland, Ohio.

Moore, Thos. W., 2604 Travis St., Houston, Texas.

Morrison, F. B., 1937 Arlington Place, Madison, Wis.

Morse, Sterne, Grant Hospital, Columbus, Ohio.

Mustard, Dr. J. W., Chatham, Ont. Canada.

Nakane, Shigeo, 5489 Cornell Ave., Chicago, Ill.

Nesser, John O., 7705 John R. St., Detroit, Mich.

Neuhausen, Ruth, Kent Chemical Laboratory, University of Chicago, Chicago, Ill.

Nordberg, Martin E., 3213 West St., Ames, Iowa.

Ota, Kenichi, Laboratory of Applied Chemistry, Imperial University, Kyoto, Japan.

Pendleton, Ferdinand H., 12 Overlook Park, Malden, Mass.

Penn, Lewis A., Room 480, Associated Oil Bldg., 79 New Montgomery St., San Francisco, Cal.

Pitts, Reginald S., 338 Wyandotte St., Bethlehem, Pa.

Pollard, Cash B., 419 Wood St., Lafayette, Indiana,

Pomeroy, Lendal W., 303 H. H. Hall, Orono, Maine.

Powers, Donald H., Graduate College, Princeton, N. J.

Reed, Robert T., 1210 W. Illinois St., Urbana, Ill.

Reimers, Ludvig, Sperry Flour Co., Ogden, Utah.

Reynolds, Albert H., 113 Marengo Ave., Forest Park, Ill.

Rice, Chester W., 3 Lowell Road, Schenectady, N. Y.

Rich, Ralph E., 2426 Clybourn Ave., Chicago, Ill.

Richards, S. Fernals, 74 Maine St., Dover-Foxcroft, Maine. Riegel, Cecilia, 4813 Sydenham St., Philadelphia, Pa. Robinson, Una, Chowan College, Murfreesboro, N. Car. Roden, Julian C., B. Division, V. P. I., Blacksburg, Va. Rosenzweig, Sender, 210 Linden Ave., Ithaca, N. Y. Rumely, Richard L., 3020 Sheridan Road, Chicago, Ill. Russell, Deborah M., State Normal School, Framingham, Mass Saier, Milton H., Thetz Xi, Stanford University, Cal. Schibsted, Helge, 33 Electric Ave., Rochester, N. Y. Schmidt, Walter Friedrich, 3149 Texas Ave., St. Louis, Mo. Schumann, C. L., 67 Tonawanda, Buffalo, N. Y. Scott, Marvin D., 2611 Huton St., Baltimore, Md. Silberman, Jacob E., 3952 Evans Ave., St. Louis, Mo. Smith, F. E., 1203 West Illinois, Urbana, Ill. Snell, Myron A., American Mineral Production Co., Valley, Wash Soderberg, Victor L., 907 So. Sixth St., Champaign, Ill. Sparberg, Max S., 4739 N. Drake Ave., Chicago, Ill. Spensley, James W., 3305 S. Michigan Ave., Chicago, Ill. Stallmann, Otto, 811 Monroe St., So. Milwaukee, Wis. Steinert, Hildur, 614 W. Washington Blyd., Urbana, Ill. Stouder, Florence Dell, 905 West Illinois, Urbana, Ill. Sudhoff, R. W., 4230 Red Bud Ave., St. Louis, Mo. Sumimoto, Seiji, Chemical Laboratory, College of Science, Imperial University, Kyoto, Japan, Swayne, William Wager, Phi Kappa Psi House, Stanford University, Cal. Thompson, Herbert O., Kewanee, Ill. Thorman, Floyd M., U. S. Gypsum Co., 205 West Monroe St., Chicago, Ill. Thornton, Nan V., 5820 Woodlawn Ave., Chicago, Ill. Tibbling, E. F., P. O. 1109, Kansas City, Mo. Tinkler, Loyal George, 54 West Monroe St., Little Falls, N. Y. Tomecko, C. G., 511 E. Healey St., Champaign, Ill. Tower, Harry E., 747 Fellsway, Medford, Mass. Turno, Irene A., 144 So. Eighth St., Newark, N. J. Tutton, H. R., Sannar Cement Factory, Makwar, Sudan. Von Wicklen, Frederick C., 119 East College St., Louisville, Ky. Walton, G. R., c/o Post Office, Houston, Texas. Walton, R. P., 1601 Fair Place, Shreveport, La. Webber, C. Sterling, 28 Bartlett Ave., Arlington, Mass. Webber, V. A., H. H. Hall, Orono, Maine. Webster, Helen, 3008 Fremont Ave., S., Minneapolis, Minn. Wells, N. W., Rice Institute, Houston, Texas. Wheeler, Daniel Gage, 107 Belleclaire Ave., Longmeadow, Mass. Wilcox, L. V., Grafton, c/o Sutter Basin Co., Cal. Williams, P. S., 200 Bush St., San Francisco, Cal. Willis, Thompson F., 620 College Ave., Columbia, Mo. Willisford, L. H., Morse Hall Cornell Univ., Ithaca, N. Y. Wilson, John Richard, 6110 Kimbark Ave., Chicago, Ill. Woods, G. W., Rice Institute, Houston, Texas. Yates, Wallace J., 3005 Benvenue Ave., Berkeley, Cal.

#### CORPORATION MEMBERS ELECTED

Boston Rubber Shoe Co., 183 Commercial St., Malden, Mass. Fansteel Products Co., Inc., North Chicago, Ill.

#### MEETINGS OF THE SECTIONS

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G. St., N. W., Washington, D. C.)

#### AMES SECTION

On November 14, Chi Che Wang, of the Nelson-Morris Institute of Medical Research in Chicago, spoke before the Section on "Blood Chemistry and the Diagnosis of Disease."

H. M. McLaughlan, Secretary

#### CALIFORNIA SECTION

The 135th regular meeting of the Section was held on November 24, when Guy S. Millberry, professor of dental chemistry and dean of the College of Dentistry of the University of California, addressed the members on the subject, "The Relation of Chemistry to Dentistry."

L. H. Duschak, Secretary

#### CHICAGO SECTION

The November meeting of the Section was addressed by C. E. K. Mees, of the Eastman Kodak Company. His subject was "Chemistry and the Motion Picture."

On December 15, Edwin O. Jordan of the University of Chicago, gave an address on "Louis Pasteur." S. L. Redman, Secretary

#### CINCINNATI SECTION

The 254 regular meeting of the Section was held on December 13, when Jerome Alexander gave an address on "Some Novel Aspects of Collodial Protection."

C. H. LUND, Secretary

#### COLORADO SECTION

On November 22, John B. Eekley, of the University of Colorado, addressed the members of the Section.

RUTH B. VERTREES, Secretary

#### COLUMBUS SECTION

At a meeting of the Section, held on November 21, 1922, the following officers for 1923 were elected: G. O. Higley, chairman; C. W. Foulk, vice-chairman; W. G. France, secretary-treasurer; W. L. Evans and C. E. Boord, councilors.

EDWARD MACK, JR., Secretary

#### CONNECTICUT VALLEY SECTION

The regular monthly meeting of the Section occurred on December 9, when C. H. Davis, of the American Brass Company, spoke on "Industrial Spectrum Analysis."

PAUL SEREX, JR., Sccretary

#### CORNELL SECTION

On December 14, F. E. Rice addressed the Cornell Section, his subject being "The Cryoscopy, Refractometry, and Electrical Conductivity of Milk."

F. E. HANCE, Secretary

#### DELAWARE SECTION

The regular meeting of the Section was held on December 20. W. K. I,ewis, of the Massachusetts Institute of Technology, spoke on "Combustion."

J. E. BOOGE, Secretary

#### DETROIT SECTION

The opening meeting for the fall season of the Section was held on November 15, when C. E. K. Mees of the Eastman Kodak Company, spoke on "The Chemistry of the Motion Picture."

S. R. Wilson, Secretary

#### EASTERN NEW YORK SECTION

At the regular meeting of the Section, held on November 17, Eugene C. Bingham, of Lafayette College, Easton, Pa., spoke on "Fluidity and its Relation to Other Physical and Chemical Properties."

The following officers were elected to take office January 1, 1923: G. R. Fonda, chairman; Arthur Knudson, vice-chairman; Edward H. Darby, secretary-treasurer; Saul Dushman and Edward Ellery, councilors; and G. M. J. Mackay, Mrs. M. R. Andrews and W. P. Davy, executive committee,

On December 14, Howard D. Clayton, of Cluett-Peabody, spoke to the members of the Section, his subject being "Textile Chemistry."

E. H. Darby, Secretary

#### HAWAIIAN SECTION

The annual meeting of the Section was held on November 15, when the present officers were reëlected for the ensuing year. A paper entitled, "A Study of Jelly Making as Concerns Hawaiian Fruits," was read by John C. Ripperton.

RONALD Q. SMITH, Secretary

#### IOWA SECTION

The regular monthly meeting of the Section was held on November 22. A paper entitled "Compressed Gases and their Uses," was delivered by A. J. Russell, of the Bettendorf Oxygen Hydrogen Co.

L. Charles Raiford, Secretary

#### KANSAS CITY SECTION

On November 22, R. F. Knappen read a paper before the Section, the subject being "Some Relations of Chemistry to Geology."

L. E. CLARK, Secretary

#### LOUISVILLE SECTION

The Section held a meeting on November 15, when C. K. Francis, of the Cosdon Company, Tulsa, Oklahoma, spoke on "Petroleum Chemistry." The following officers for 1923 were elected: C. E. Bales, chairman; T. J. Bosman, vice-chairman; C. E. Geiger, secretary-treasurer; A. W. Homberger, councilor.

C. E. Geiger, Secretary

#### MAINE SECTION

At the meeting of the Section, held on November 10, the following officers were elected for 1923: C. A. Brautlecht, president; J. M. Bartlett, vice-president; N. E. Woldman, secretary-treasurer.

On December 8, B. F. Brann addressed the Section on the subject "Nitrogen Fixation."

N. E. Woldman, Secretary

#### MARYLAND SECTION

The 60th meeting of the Section occurred on November 24, and was a joint meeting of the Maryland and Washington, D. C. Sections. In the afternoon an inspection of the American Sugar Refinery, at Locust Point, Md., was made, and in the evening Carl F. Huttlinger, superintendent of the American Sugar Refinery, addressed the meeting on "The Process of Refining Sugar."

The following officers for 1923 have been elected: S. T. Powell, chairman; Carl Haner, Jr., vice-chairman; Adolph Harvitt, secretary-treasurer; A. E. Marshall, A. A. Backhaus and Neil E. Gordon, councilors; J. C. W. Frazer, M. D. Scott, W. A. Taylor, A. H. Warth, W. B. D. Penniman, and J. H. Wolfe, executive committee.

ADOLPH HARVITT, Secretary

#### MICHIGAN AGRICULTURAL COLLEGE SECTION

On November 10, W. Lee Lewis, of Northwestern University, addressed the meeting of the Section, his subject being "The Organic Chemist."

The Local Section held its annual banquet on the evening of December 8. Howard B. Lewis, of the University of Michigan, spoke on "Recent Developments in the Study of the Role of Proteins in Nutrition."

E. F. ELDRIDGE, Secretary

#### MILWAUKEE SECTION

The following officers have been elected for 1923: C. H. Hall, chairman; C. N. Davidson, vice-chairman; A. A. Chambers, secretary; L. E. Power, treasurer; R. N. Bauer and C. R. McKee, councilors.

On November 17, W. Lee Lewis, of Northwestern University, addressed the members of the Section on the subject, "The Organic Chemist at Work."

O. A. CHERRY, Secretary

#### MINNESOTA SECTION

The 104th regular meeting of the Section occurred on November 27, when Victor Lenher, of the University of Wisconsin, gave a lecture on "Selenium Oxychloride."

On December 13, F. J. Alway, gave a paper on "The Agricultural Uses of Peat," and C. I. Wallfred, a paper on "Peat as an Industrial Fuel."

L. M. HENDERSON, Secretary

#### NEBRASKA SECTION

The 106th meeting of the Section occurred on November 28. The subject of the meeting was "Unpublished Researches from the University of Nebraska Chemical Laboratory," presented by Fred W. Upson, Ernest Anderson and T. J. Thompson.

S. B. Arenson, Secretary

#### NEW HAVEN SECTION

A meeting of the Section was held on December 5. Following a dinner in the evening, S. K. Becker of the U. S. Aluminum Company, spoke on "Aluminum Casting Alloys."

BLAIR SANTON, Secretary

#### NORTHEASTERN SECTION

The 180th meeting of the Section occurred on December 8, with the following program: "Petroleum Research," by C. O. Johns, of the Standard Oil Company; and "Recent Developments in Catalysis," by H. W. Underwood, Jr., of the Massachusetts Institute of Technology.

In lieu of the regular January meeting of the Section, a smoker to the visiting members of Section C of the American Association for the Advancement of Science, was given on December 29.

E. B. MILLARD, Secretary

#### PHILADELPHIA SECTION

On November 17, W. D. Collins of the U. S. Geological Survey, delivered a lecture before the members of the Section, his subject being "Hardness of American Water Supplies."

The regular monthly meeting of the Section was held on December 21, when John H. Muller, of the University of Pennsylvania, gave a lecture on "Germanium."

J. HOWARD GRAHAM, Secretary

#### PITTSBURGH SECTION

The 182nd meeting of the Section was held on November 16. The paper of the evening was by C. M. Johnson, on "Some Corrosion-Resisting Steels."

On December 21, W. M. Corse addressed the members, his subject being "The Manufacture and Properties of Nickel."

E. S. STATELER, Secretary

#### PUGET SOUND SECTION

The regular monthly meeting of the Section was held on November 23, when E. Z. Lynn, of the College of Pharmacy, University of Washington, read a paper on "The Manufacture of Zinc and Barium Products."

The following officers have been elected for 1923: Thomas G. Thompson, chairman; A. G. Bissell, vice-chairman; R. W. Ellison, secretary; G. C. Howard, treasurer; and H. K. Benson, councilor.

R. W. Ellison, Secretary

#### PURDUE SECTION

The Section held a meeting on November 16, at which time C. E. K. Mees of the Eastman Kodak Company, gave an illustrated lecture on "Chemistry and the Motion Picture."

MARGUERITE G. MALLON, Secretary

#### RHODE ISLAND SECTION

At the meeting of the Section, held on November 24, Augustus H. Fiske, chief chemist of the Rumford Chemical Co., spoke on chemical problems with which he has been connected.

A meeting of the Section was held on December 22, when A. N. Dana, of Yale University, lectured on "Some of the Very Apparent Advantages of Dyeing in Wound Form."

Nelson Barlow, Secretary

#### ROCHESTER SECTION

The 144th regular meeting of the Section occurred on November 20, when W. K. Lewis, of Massachusetts Institute of Technology, spoke on "Combustion."

The 145th regular meeting of the Section was held on December 4. Thomas Midgley, Jr., of the General Motors Research Corporation, gave a paper on "A Elementary Discussion of Research."

B. M. Billings, Secretary

#### SAINT LOUIS SECTION

Short papers, as follows, were presented at the meeting of the Section, held on December 4: "A New Form of Melting Point Apparatus," by H. A. Bell; "Some Difficulties in the Qualitative Detection of Morphine," by B. H. St. John; and "The Customs Chemist," by Fred West.

At this meeting the following officers for 1923 were elected: P. A. Shaffer, chairman; R. R. Matthews, vice-chairman; H. A. Carlton, secretary; B. H. St. John, treasurer; A. C. Boylston, C. W. Cuno and E. J. Sheppard, councilors.

H. A. Carlton, Secretary

#### SAVANNAH SECTION

At the first fall meeting of the Section, held on November 2, Herbert S. Bailey gave an extensive report on the Pittsburgh meeting. The following officers for 1923 were elected: Philip McG. Shuey, chairman; John N. Everson, vice-chairman; Herbert P. Strack, secretary; and Herbert S. Bailey, councilor.

Herbert S. Strack, Secretary

#### SOUTHERN CALIFORNIA SECTION

On December 14, Richard C. Tolman, of the California Institute of Technology, addressed the meeting of the Section, his subject being "Modern Ideas as to the Structure of the Atom."

MARK WALKER, Secretary

#### SYRACUSE SECTION

The 164th regular meeting of the Section was held on December 8. Horace C. Porter spoke on "Coal Carbonization and the World's Fuels." W. B. Hicks, Secretary

#### UNIVERSITY OF ILLINOIS SECTION

The regular meeting of the Section occurred on November 21. W. H. Rodebush of the University of Illinois, spoke on "The Production of Helium for Military Purposes." The following officers for 1923 were elected at this meeting: J. H. Reedy, chairman; A. M. Buswell, vice-chairman; D. T. Englis, secretary; Edith Nason, treasurer; Roger Adams and B. S. Hopkins, councilors.

D. T. Englis, Secretary

#### UNIVERSITY OF MICHIGAN SECTION

On December 14, H. B. Lewis, of the University of Michigan, addressed the members of the Section, his subject being "Some Recent Advances in the Role of Proteins in Nutrition."

C. C. Meloche, Secretary

#### VIRGINIA SECTION

The 53rd regular meeting of the Section occurred on November 10, when Robert N. Pease, of the University of Virginia, addressed the members on the subject "Recent Developments in Contact Catalysis."

W. G. CROCKETT, Secretary

#### WASHINGTON, D. C. SECTION

The 335th meeting of the Section occurred on November 24, and was a joint meeting, in Baltimore, Md., with the Maryland Section.

The 336th meeting of the Section was held on December 14, when Wm. Mansfield Clark spoke on "Oxidation-Reduction Indicators." The following officers for 1923 have been elected: William Mansfield Clark, president; J. B. Reed, secretary, H. W. Houghton, treasurer; W. W. Skinner, R. B. Sosman, R. C. Wells, W. D. Collins, and F. C. Cook, councilors; A. Seidel, L. H. Adams, E. T. Wherry, V. K. Chesnut, F. W. Smither, and R. O. E. Davis, executive committee.

J. B. Reed, secretary

#### WESTERN NEW YORK SECTION

On November 14, K. W. Stenstrom, of the New York State Institute for the Study of malignant Disease, addressed the Section, his subject being "Radium, its Value in Theory and Practice."

At the regular monthly meeting, held on December 5, J. C. McLennan, of the University of Toronto, gave a lecture on "The Structure of Atoms." R. W. Hess, Secretary

#### WISCONSIN SECTION

On November 15, Arnold Sommerfeld of the University of Wisconsin, addressed the Section. His subject was "Atomic Structure and the Periodic Law."

At the regular monthly meeting, held on December 13, E. C. Sherrard, of the University of Michigan, spoke on "Hydrolysis of Wood."

JESSE E. DAY, Secretary

#### DECEASED

Frederick North Crawford, 159 High St., Middletown, Conn. Died, November 4, 1922. Spencer Baird Newberry, 818 Engineers Building, Cleveland, O. Died, November 28, 1922. William E. Spandon, Columbia University, New York, N. Y. Died, November 17, 1922.

## Proceedings

### Report of the Secretary of the American Chemical Society for the Year 1922

The American Chemical Society is on the upgrade again in its active membership although the number at the end of this year differs little from that of 1921.

This is due to the fact that under the Constitution members are carried as members without journals or two years after they have ceased to pay dues, unless their resignation is received, in the expectation that they will remove their delinquency. Accordingly, at the end of 1922 a considerable number will be dropped from the membership count who really have not been of any assistance to the Society during the last two years. The industrial activity of the country is increasing and with it chemists who, during the depression, lost their positions are again finding profitable employment. In this returning prosperity the American Chemical Society itself is again beginning to share. During the depression the Society has not been idle. Strengous efforts have been put out to enlighten the country regarding the value of chemists and chemistry to the community. These efforts have met with a reasonable measure of success. Lectures by prominent members have been given before chambers of commerce, women's clubs, local sections of the Society, and have been transmitted by radio in order to enlighten the people as to the value of chemistry in everyday life. Six lectures by prominent members of the Society on special topics were given before the students and officers of the Naval Academy at Annapolis and of the Military Academy at West Point. The Society has received expressions of sincere appreciation for its efforts toward a better understanding of chemical problems by our military establishment from both academies. Similar lectures for the winter of 1922-1923 are now being arranged.

Our journals have increased in quality and usefulness. More research has been published than ever before. More pages have appeared in 1922 in the Journal of the American Chemical Society and Chemical Abstracts than have been printed in any previous year. The material in these pages, owing to the increased amount of material available has been scanned more severely so that quality has increased with quantity. The new editor of the Industrial and Engineering Chemistry has distinctly improved the appearance and the influence of that publication although its size has remained unchanged. Our advertising managers, even during the depression when other technical journals had been losing advertising, steadily and decidedly increased the number of our advertising pages. The net income from advertising in 1922 was much larger than ever before. As previously pointed out, this is simply a dividend returned to our members in the extra quality of the service the Society is able to render. The News Service is showing increased influence. Its releases are more widely used by the secular press. It has been also of special service to technical magazines. The News Service needs cooperation from our members in getting the right kind of material to send to the daily press and the manager of the News Service will gladly hear from our members regarding any available material. The News Service has already greatly diminished the amount of chemical quackery appearing in the public press so that most of the information regarding chemistry now printed can be depended upon. The correctness of the information furnished is the first thought of our News Service.

The Society has received special recognition from the War Department for, by the unsought request of that Department, a committee of the Society has been appointed to cooperate with the officers of the War Department in all matters requiring expert chemical advice.

The Society has entered into an agreement with the Chemical Society of London and the Faraday Society to publish under joint auspices the Journal of Physical Chemistry. Although the management of this journal will be quite independent, arrangement will be made where members of the three societies will obtain a reduced subscription price. The continuation of the Journal of Physical Chemistry under these new conditions is made possible by a guarantee of \$10,000.00 per year for five years from Mr. Francis P. Garvan in behalf of the Chemical Foundation and himself personally.

A medal, known as the Priestley Medal, has been established to be awarded annually for distinguished services to chemistry and will be awarded first at the New Haven Meeting of the Society April 3-7, 1923.

The Society has been made custodian, through the influence and recommendation of one of its Past Presidents, William H. Nichols, of a prize of \$25,000.00 to be awarded annually to some American chemist. The details of award are now under consideration.

Two successful meetings have been held during the year; one at Birmingham and one at Pittsburgh. They were well attended and added materially to the cause of chemistry both locally and throughout the country. The Sections of Cellulose Chemistry and Petroleum Chemistry have been given divisional status and have become enthusiastic and active divisions, progressive and well attended.

The American Chemical Society monographs are progressively successful. Nine monographs have been issued. Other important monographs will soon be issued and still others are in preparation. This new departure of the Society is already an assured financial success and the monographs are taking the stand in the chemical world which the Society would wish to see for any publication bearing its insignia.

In legislative matters the Society has been acting only under the strict control and direction of the Council or by the Committee on National Policy. The status of industrial alcohol has been distinctly improved, chiefly by enlarging the understanding of the absolute necessity for the use of alcohol in chemical manufacture as distinguished from its beverage use. The Lampert Bill for the improvement of the Patent Office and employees therein has been passed and signed by the President and the Society has received the courteous acknowledgment of the Commissioner of Patents for its successful efforts. The Society is active in supporting legislation in favor of Chemical Warfare Service and in attempting to impress those in authority with the absolutely essential support of research if the country is to be prepared to defend itself against the unscrupulous. The Society was successful in its efforts in assisting the protection of American manufacturers of chemicals and chemical apparatus. The effort put out by the chemists of the country, including the American Chemical Society, for proper legislation for the continuation of our organic chemical industry was not successful on account of skillfully prepared false propaganda and the selfish political activity of a minority consuming industry who preferred to put their own material interests before the country's chemical preparedness or its material welfare. Great progress was, however, made in educating the public, as well as the people's representatives, to a correct understanding of the value of chemistry, and the publications of the last Congress contained probably more material bearing upon true chemical science and chemical industry than all the publication of previous Congresses put together. A successful conference was held at the Pittsburgh Meeting on the Metric System, and the Society's representatives appeared in favor of the Ladd Bill to fix the Metric System of Weights and Measures as the standard for the United States. The Metric System is making distinct and rapid progress in the appreciation of our people. Its adoption, however, is, of course, expected to be slow, and the Society can only continue to be one of the helps towards its final acceptance.

The membership of the Society as reported last year was 14,318. The membership of the Society on December 31, 1922, was 14,400. Statistics follow:

Honorary Members	11
Life members	20
Corporation members	230
Members	14,150
	-
Total, December 31, 1922	14,400

The number of members not in arrears registered in the local sections on November 30, 1921, was 10,679. The number on November 30, 1922, was 9,947. The number in each section for 1921 and 1922 is noted below:

Local section	Number of paid mem- bers, 1921	Number of paid mem- bers, 1922	Cash retained from balance, 1921	Total receipts 1922
Alabama	44	38	\$ 67.50	\$ 67.50
Ames	48	40		70.50
Arkansas	30	23	.15	50.00
California	382	332		200.00
Central Texas	77	53		96.25
Chicago	801	716		600.75
Cincinnati	240	211		200.00
Cleveland	325	309	9.55	243.75
Colorado	91	71	34.98	84.98
Columbus	94	93		98.25
Connecticut Valley	112	103		135.00
Cornell	50	44	7.50	73.50
Delaware	175	141	40.08	175.00
Detroit	138	130		138.00
Eastern New York	101	86	3.27	126.25
Georgia	47	37	3.62	53.62
Hawaiian		24		50.00
Indiana	144	139		156.25
Iowa	77	88	2.56	96.25
Kansas City	182	169	67.49	182.00
Lehigh Valley	91	81	31.70	113.75
Lexington	23	24		50.00
Louisiana	81	81	91.25	91.25
Louisville	24	19		
Maine	49	41	15.25	68.75
Maryland	221	208	10.35	173.25
Michigan Agricultural College	36	35		54.00
Midland	25	24	19.93	50.00
Milwaukee	138	133		156.60
Minnesota	165	152	50.14	165.00
Nashville	. 26	15		50.00
Nebraska	. 31	25	11.12	61.12
New Haven	. 84	79		105.00
New York	2,032	1,842	61.64	1,441.64
North Carolina	. 53	48	3.64	53.64
Northeastern	. 844	820	7.47	633.00
Northern Indiana		46		50.00
Northern Intermountain	. 21	18	33.00	33 .00
Northern West Virginia		29		•••••
Oklahoma	. 89	62	14.22	64.22

Local section	Number of paid mem- bers, 1921	Number of paid mem- bers, 1922	Cash retained from balance, 1921	Total receipts 1922
Omaha	37	24	12.56	12,56
Oregon	38	51	20.92	57.00
Philadelphia	683	624	.28	512.25
Pittsburgh	472	434		300.00
Puget Sound	75	72	11.75	93.75
Purdue		38		50.00
Rhode Island	107	98	.99	143.75
Rochester	144	110		130.00
St. Louis	206	195	.33	200.00
Sacramento		25		50.00
Savannah	. 25	22	2.51	27.51
South Dakota	17	19	43.60	43.60
Southeast Texas	54	53	19.94	19.94
South Jersey	42	32		63.00
Southern California	230	249	28.44	200.00
Syracuse	148	111		148.00
Toledo	46	44	.38	69.00
University of Illinois	153	138	12.93	112.93
University of Michigan	66	70	17.35	77.35
University of Missouri	23	26	9.83	9.83
Vermont	27	25		50.00
Virginia	107	104		133.75
Washington, D. C	384	398	41.72	288.00
Western New York	248	210	72.99	186.00
Wisconsin	156	146	3.75	138.75
	10,679	9,947	\$886.68	\$9,429.04

The table gives a summary of the sectional accounts for the year, shows the number of members in each Section for 1921 and 1922, the funds held over from 1921 account, and the total funds (which include the balances) charged to the 1922 account.

During the year the Society added the Hawaiian, the Sacramento and the Northern West Virginia to its local sections, and discontinued the South Dakota Section.

During the past two fiscal years, December 1, 1920, to November 30, 1922, the Secretary has made the following collections:

	1921	1922
Membership	\$190,270.00	\$175,910.00
Subscriptions, non-members	21,154.26	21,292.48
Back numbers	6,295.62	6,139.44
Reprints	1,925.17	3,739.10
Postage	3,911.56	4,226.23
Interest	946.60	1,144.32
Exchange and miscellaneous	.56	.93
Directory	49.00	28.50
Decennial Index to Chemical Abstracts	610.00	565.00
	\$225 162 77	\$212.046.00

These amounts were duly transmitted to the Treasurer of the Society.

Full and explicit details of the business management of the Society for many years past will be found in the January 20 issue of the Industrial and Engineering Chemistry.

Several sets of Chemical Abstracts have been completed and sold during the year as well as complete sets of the Industrial and Engineering Chemistry. Complete sets of the Journal of the American Chemical Society can no longer be sold as it is impossible to fill in certain early numbers which are exhausted. Nevertheless, the Society has sold a number of incomplete sets to the extent that they could be completed, and there is still a demand for such, as full sets are almost unobtainable. The stock has been kept in good condition by the purchase of numbers needed to complete full volumes, but many volumes are already sold out and a number of issues of all three of our journals are nearing exhaustion.

Back numbers are mailed direct from Easton, Pa., on orders sent through the Secretary's office. The following is a summary of the back numbers sent out by the Secretary during the year, together with the present stock of journals:

Copies of the Society's publications sent out from January 1, 1922 to December	
31, 1922, aside from mailing lists	47,399
Copies of the Journal of the American Chemical Society in stock	21,893
Copies of Chemical Abstracts in stock	24,106
Copies of the Industrial and Engineering Chemistry in stock	22,187
Copies of the General Index, Vols. 1-20, J. A. C. S. in stock	70
Copies of the Anniversary Number in stock	87
Volumes of Decennial Index in stock	305

Respectfully submitted, Charles L. Parsons, Secretary

# Report of the Editor of the Journal of the American Chemical Society for the Year 1922

The number of articles and the number of the pages devoted to them and to the Proceedings of the Society during the past five years, exclusive of the indexes and the tables of contents, have been as follows:

		3	Numbe	r				Pages		
	1918	1919	1920	1921	1922	1918	1919	1920	1921	1922
Proceedings						112	162	168	128	117
Physical and Inorganic	114	107	180	179	191	1023	1053	1695	1688	1844
Organic and Biological	106	116	122	154	148	906	1089	936	946	1082
Book Reviews	21	29	54	57	47	30	31	59	70	48
								· ; <del></del> ;		
Total						2071	2335	2858	2832	3091

This table shows that in the past year for the first time, the maximum number of pages, 2944, reached in 1916, has been equaled.

The insistent demand for space in the Journal has continued. Moreover, a good deal of material accumulated during the printers' strike of 1921 and was carried over into 1922. Worst of all, the low state of the Society's finances forced the Directors to disapprove any increase in the size of the Journal over the preceding year. The outlook at the beginning of the year was, therefore, far from promising. Fortunately, however, a considerable decrease in the expense of printing was achieved, and as a result it was possible to publish the slightly increased number of pages indicated above. The average length of the articles in 1922 was 8.6 pages as compared with 8.2, 8.7, and 9.6 in 1921, 1920, and 1919.

At the end of the year, Associate Editors C. A. Browne and W. F. Hillebrand were retired by lot. The Editor wishes to express his own and the Society's appreciation

of their long, able and unselfish services. Roger Adams and E. W. Washburn were elected by the Council to the vacancies thus created.

ARTHUR B. LAMB, Editor

# Report of the Editor of Chemical Abstracts for 1922

The 1922 volume of Chemical Abstracts contains 23,212 abstracts, an increase of 3,736 over the 1921 volume. Of the abstracts 18,070 are of journal or like papers and 5,142 of patents. The number of titles of new or revised books in this volume is 886. The edition has averaged about 13,500 copies per number.

The average lengths of abstracts of papers and of patents in 1922, with comparative figures for the preceding five years, are shown in the following table, the unit being a page.

	1922	1921	1920	1919	1918	1917
Paper abstracts	0.190	0.218	0.223	0.244	0.220	0.251
Patent abstracts	0.086	0.098	0.107	0.115	0.099	0.108

The general average length for abstracts of papers for all of the preceding volumes is 0.225 page; that for patent abstracts for 13 preceding volumes (data are not available for volumes 1 and 2) is 0.98 page. The decrease in length of 1922 abstracts amounts to 15.5% for abstracts of papers and 12.2% for patent abstracts as compared with the general average of preceding volumes. This decrease, a very considerable one in view of the fact that brevity has always been emphasized, has been necessary in order that our efforts to cover the field completely might be carried out in the face of necessary space limitations. This necessity, a product of such circumstances as increased printing costs and the growth of the literature, is much to be regretted for there is no doubt that abstracts could be made more useful if it were possible to make them more informational. It may be pointed out, however, that every effort has been made to keep the briefer abstracts complete in the descriptive sense; this makes it possible for the indexing to be thorough. The indexing, particularly the subject indexing, has received continued special attention and no reduction has been made in the space devoted to the indexes, in the belief that the journal should be as nearly as possible a complete guide to the literature even though it cannot serve as the direct source of as much information as is desirable. It has still been possible to give suitable data and other information in most abstracts rather than merely references to them. The impression should not be gained that abstracts have had to be altered greatly; the point is that the tendency has had to be in the wrong direction. It will always be wise carefully to conserve space, but it will be a good thing for the journal when abstracts can be reasonably lengthened.

To provide just that much more space for chemical information the practice during 1922 has been to eliminate from abstracts the addresses of authors (laboratories where work reported was done). Addresses are helpful in appraising work and are useful in the obtaining of reprints. It is hoped, as has been requested by a number of chemists, that addresses can be reinstated eventually. The vote in response to a questionnaire on the subject was 72 to 20 in favor of devoting the space to chemical information so long as present conditions hold. In most cases initials only have been given in all but the surname part of author names. Abstractors' names are reduced to initials only by the printer when a line can thus be saved.

A point which has frequently been raised when the length of abstracts is under consideration is the relatively great length of the abstracts of organic papers. The reason these abstracts have a considerably higher average of length than the others lies in the

fact that, from the nature of things, a good deal more space is required for an adequate abstract of an organic paper than for an abstract on the same level of effectiveness and usefulness in any other field. The same is true of the indexing. Such a record as Chemical Abstracts constitutes would certainly not be complete and satisfactory if it did not at least briefly describe and index new compounds, and organic papers almost always contain descriptions of a number of such compounds. A markedly abbreviated style is used and the information given is limited. Another condition which affects the situation somewhat is the fact that organic papers are almost always all chemistry; there are no brief borderline abstracts to bring down the average. There is of course no desire to overemphasize any phase of chemistry. The 1922 organic abstracts are 18.5% shorter than those of 1921.

The field to be covered has grown considerably during the past few years owing to the fact that the physicists have been working more and more on subjects of distinct chemical interest, such subjects as atomic structure, radioactivity, gaseous ionization, crystal structure, spectroscopy and electron theory occupying their attention to a very large extent. There is so much direct chemical interest in these studies by physicists that it is necessary now to cover the physical journals almost as fully as the chemical ones. In this field and in the biological field (there are hundreds of biological and medical journals to be watched) it is particularly difficult to decide where to draw the line. The policy is to abstract in case of doubt, the abstracts of doubtful papers being made very brief as a rule.

Continued effort has been made to keep the nomenclature in Chemical Abstracts good. This is particularly true with reference to the systematic naming of compounds in the indexing.

In the October 20th number a revised "List of Periodicals Abstracted" was published. It gives information concerning 1010 publications. A new feature is the inclusion of location data for 172 libraries. This information was obtained through the coöperation of the National Research Council. There is much evidence that it is proving very useful. In helping users of Chemical Abstracts to obtain original papers it is serving to make up in part for the briefer abstracts which have been necessary.

It has been arranged to issue the 1922 indexes (author, subject and formula) in two parts, the first part consisting of the Author Index and the second containing the other two indexes. This seemed desirable because of binding difficulties resulting from the increased number of pages. The Author Index appeared near the middle of January and Part 2 is expected to go into the mails about February 20th. While quality of course comes before speed in the work on these indexes, which really present a rather big task in the printing as well as in the compilation and editing, every effort is made to get them into the hands of the users at the earliest possible time. The amount of work necessary in the compilation of the subject index in its present improved form and the addition of the Formula Index will not permit of the issuance of the complete index early in January, as was accomplished several years ago, but the 1922 indexes will be prompter than any since the Formula Index was added and it is expected that still better time can be made in another year if present plans can be carried out. The value of prompt indexes is recognized.

After many years of service as an abstractor and assistant editor Gerald L. Wendt has relinquished the reins as head of the section on Subatomic Phenomena and Radiochemistry to S. C. Lind, a good and faithful abstractor since the early days of the journal. Dr. Wendt deserves great credit for his work in developing this section. Paul E. Howe has taken over the work of Assistant Editor in charge of the section on Biological Chemistry, replacing William J. Gies, Hattie L. Heft and Edgar G. Miller, Jr.

Dr. Gies gave up the work after ten years of notably valuable service in which he was capably assisted by Miss Heft and Dr. Miller during the latter part of this period. B. M. Duggar has taken Carl L. Alsberg's place in charge of the sub-section on Botany. Dr. Alsberg's appreciated services also extended over a period of ten years. C. N. Frey is now in charge of the section on the Fermentation Industries, formerly handled by H. S. Paine, whose work for a number of years as an unusually capable abstractor from a variety of difficult languages well deserves our additional appreciation. Clarence J. West has assumed the place in charge of the Cellulose and Paper section made vacant by the resignation of A. D. Little, the beginning of whose valuable services for Chemical Abstracts dates back to the first appearance of the journal in 1907. The gratitude of all of us is due the retiring assistant editors and abstractors and the many now active in the work for their unselfish service. Their willingness to devote a lot of time to Chemical Abstracts with little or no pay furnishes a fine example of altruism. It would be difficult to overemphasize the value to the journal of this spirit of service. The editor wishes to express his appreciation to all again at this time.

Statistics for the various sections follow. Data are given for 1921 as well as 1922 since the delays caused by the printers' strike made it impossible to supply such figures in the report last year.

		1921	1	922
	No. of pages	No. of abstracts	No. of pages	No. of abstracts
Apparatus	.46.1	295	31.4	255
General and Physical Chemistry	234.2	1050	287.7	1508
Subatomic Phenomena and Radio-				
chemistry	170.7	750	174.3	904
Electrochemistry	71.4	415	53.8	343
Photography	12.8	94	11.6	88
Inorganic Chemistry	56.6	190	61.1	244
Analytical Chemistry	108.1	477	105.0	512
Mineralogical and Geological Chemistry	79.3	454	86.9	661
Metallurgy and Metallography	141.9	908	159.2	960
Organic Chemistry	689.8	1163	686.2	1421
Biological Chemistry	740.1	3672	773.5	4655
Foods	88.9	534	83.7	539
General Industrial Chemistry	38.7	317	37.6	262
Water, Sewage and Sanitation	55.2	430	51.4	448
Soils, Fertilizers and Agricultural Poisons.	82.3	472	76.2	464
The Fermentation Industries	26.1	147	23.7	137
Pharmaceutical Chemistry	76.4	439	89.5	595
Acids, Alkalies, Salts and Sundries	40.5	320	40.2	333
Glass, Clay Products, Refractories and				
Enameled Metals	45.6	277	66.1	418
Cement and Other Building Materials	22.1	137	35.3	218
Fuels, Gas, Tar and Coke	110.1	584	142.5	856
Petroleum, Asphalt and Wood Products	45.4	246	48.5	260
Cellulose and Paper	41.5	314	48.0	316
Explosives and Explosions	35.9	140	39.6	159
Dyes and Textile Chemistry	44.2	263	53 . 1	369
Paints, Varnishes and Resins	41.7	206	29.7	198
Fats, Fatty Oils and Soaps	65.5	298	52.3	310
Sugar, Starch and Gums	54.1	319	41.1	276

Leather and Glue	31.9	160	36.2	229
Rubber and Allied Substances	25.2	140	25.6	132
Total not including patents	3322.3	15.211	3451.0	18.070
Patent abstracts	421.3	4,265	447.0	5,142
	Andrew Property Company	-	*****	
	3743.6	19,476	3898.0	23,212
Book titles	47.2	975	41.4	886
Headings, blanks and cross references	140.5		141.8	
	3931.3		4081.2	

Respectfully submitted, E. J. Crane

# Report of the Editor of Industrial and Engineering Chemistry

The journal of Industrial and Engineering Chemistry has continued to place emphasis upon the publication of original papers, primarily upon research and chemical engineering, to which something more than 73 per cent. of its pages have been devoted. The discussion of industrial and plant problems has been made a feature and emphasis has been placed upon original research work. The September number, devoted to many reports of progress, was reprinted in phamphlet form and distributed to libraries of chambers of commerce. Two important symposia were published, one on distillation and the other upon automatic process control.

A number of new features have been introduced. Decided improvements have been made in the typographical features of the publication, synopses of the longer articles have been made a regular feature, letters have been secured from Canada and Japan, economic features have been stressed in special articles, lists of industrial films added, and the market reports expanded. A series on American contemporaries has been initiated and that part of the Journal devoted to government and new publications, book reviews, and scientific societies has been revised. The index for 1922 has been made more compact, and there has been constantly in mind the desirability of placing in the Journal more and more material of permanent interest and value.

Early in the year all the sections were invited to appoint staff correspondents and these correspondents have been of great assistance not only in supplying information, but in obtaining comments and criticisms. The Advisory Board has been active and has contributed much to any success which has been achieved. The editor has visited more than a third of the local sections and from these conferences has obtained much that will help him in conducting the Journal in accordance with the interests of readers. Further trips are in contemplation.

The editorial office performs a variety of service for industrial readers, advertisers, and local sections. The offer to act as a Washington Bureau in procuring special information has been widely accepted. The instructions of the Council in matters pertaining to legislation have been faithfully carried out and activities on numerous committees have all been in the interests of American chemistry.

The Advertising Department has been aggressive and is to be complimented upon the showing made. The Eschenbach Printing Company has given cooperation which left nothing to be desired, and through efficient management has enabled very substantial savings to be made in the cost of printing.

Analysis discloses that 1 per cent. of the space of the Industrial and Engineering Chemistry has been devoted to tables of contents; 1.7 to the index; 2.83 to

editorials; 21.33 to notes and correspondence, scientific societies, foreign letters, Washington notes, government and new publications, book reviews, market reports and other miscellaneous material; and 73.78 to original papers and other contributed articles or research and industrial chemistry.

The following comparison with 1921 may be made:

Number of Separate Articles		
•	1921	1922
Editorials	53	. 97
Original Papers	310	316
Foreign letters, Market reports, Notes, Scientific		
societies, etc	105	141
Book Reviews	67	81
	-	<del></del>
	535	635

The office equipment has been repaired and put in first class condition, worn typewriters replaced, and surplus property sold. The reference journal volumes have been bound and the net assets of the Society increased in these several ways.

Preliminary figures indicate these totals:

	1921	1922
Gross cost, all items except advertising	\$81,256.20	\$69,072.25
Cost of printing advertising	38,105.37	28,229.42
Net return from advertising	39,034.09	50,000.00

Gratitude is expressed to authors whose coöperation has made it possible to maintain the high standard of the Industrial and Engineering Chemistry, to advertisers without whose valued support not only this publication but all the publications of the Society would suffer, and to the many reviewers who have generously given their time for the consideration of manuscripts and new books.

Authors are asked to write as compactly as possible and to omit nonessential material, remembering that shorter articles are read with greater interest by a larger number, thus advancing the interests of both author and reader. The approximate percentage of total circulation represented by each of the several special interests served by the Journal has been determined, and in so far as is possible articles for each number will be selected with a view to serving these several special groups.

# NEWS SERVICE

The News Service has been conducted with several definite objects in view. These may be designated as the promotion of research, the exposure of fakes, the development of special interests represented by divisions of the Society, publicity for the semiannual meetings, assistance to local sections, and the furtherance of legislative matters in accordance with the instructions of the Council.

A special effort has been made to have the nontechnical press seek the advice of specialists through the News Service before printing sensational announcements, and where this could not be forestalled, correct explanations and data have been given through releases. Not only through newspapers but through trade publications, an effort has been made to interest definite groups of manufacturers in what research may be expected to do for them. An illustration of this is the use by 67 newspapers of an article a column in length on the opportunities in the leather industry for the application of chemistry.

The instructions of the Council relative to service at the general meetings have been faithfully executed. Abstracts in so far as they could be procured preceding the two general meetings were prepared and supplied to the technical and daily press. This service is being steadily improved and, beginning with the New Haven meeting, it is proposed to extend it to certain division members as provided by their division by-laws. While many local sections have acted through successful publicity committees, others have requested and been given assistance by the News Service with the result that greater attention is paid locally to the activities of chemists.

An increase in publicity has been obtained with a decrease in expenditure.

	Expenses	Inches of publicity measured
1917	\$ 500	no record*
1918	1,850	5,000
1919	2,069	9,000
1920	8,078.69	21,000
1921	12,792.93	70,000
1922	10,306.12	79,101

* It will be remembered that in 1917, 1918 and 1919 the News Service was operated as a Society committee activity.

There have been 88 separate releases, not counting items printed in the Chemical Round Table, so that the total items circulated are in excess of 100. The clippings received in the office number 8,107 and measure 79,101 inches. Much of the material is rewritten by the press before use, and if the American Chemical Society is not mentioned, clippings are not received. Further, no clipping bureau obtains all the clippings. It is fair to estimate that the 79,101 inches represent only a part of the total publicity obtained.

A more accurate system for checking results has been developed so that the date upon which the release was issued, the author of the story, its subject, the number of clippings received, and their total measurement can be reported. Exhibits are on file and are always open for the examination of those interested.

The publicity work of the Society is just beginning to bear fruit. The results of the last half of 1922 clearly show an inclination on the part of the press to give more and more space to scientific news, notwithstanding the increased demand upon space. Frequently interesting releases which are not closely connected with definite dates are used long after the official mailing and we are still receiving clippings of articles released in January 1922.

The News Service has assisted in creating a favorable attitude on the part of the public toward research. Still greater results can be obtained if increased coöperation can be secured from the research and industrial chemists. Many news items remain unused because men engaged in the work do not recognize their news value. There is a greater demand for authentic scientific news in newspaper language than can be met with the material ordinarily received and the News Service not only heartily thanks those who have been of great assistance during the work of the present year, but bespeaks still further efforts in 1923.

H. E. Howe, Editor

# COUNCIL

MEMBERS ELECTED BETWEEN DECEMBER 15, 1922 AND JANUARY 15, 1923

Abe, Ryonosuke, Laboratory of Engineering Chemistry, Imperial University, Kyoto, Japan. Ackley, Adrian L., Phi Eta Kappa, Orono, Maine.

Affleck, John K., 2 Spading Road, Toronto, Ont., Canada.

Alwood, Fred W., 609 E. Johnson St., Clinton, Ill.

Amidon, Geo. W., American Institute of Baking, 1135 Fullerton Ave., Chicago, Ill.

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# CORPORATION MEMBERS ELECTED

The International Nickel Co., 67 Wall St., New York City. Thompson's Malted Food Company, Waukesha, Wis.

# MEETINGS OF THE SECTIONS

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

### CALIFORNIA SECTION

The 136th regular meeting of the Section occurred on December 29, 1922, when Oliver C. Ralston, superintendent of the Pacific Experiment Station of the U. S. Bureau of Mines, addressed the members, his subject being "Aluminum Chloride, its Manufacture and Uses."

At the above meeting, the following officers for 1923 were elected: Carl L. Alsberg, chairman; C. W. Porter, vice chairman; L. H. Duschak, secretary-treasurer; W. C. Bray, R. A. Gould, J. H. Hildebrand and Arthur Lachman, councilors.

L. H. Duschak, Secretary

# CENTRAL TEXAS SECTION

At the annual fall meeting of the Section, held at College Station, Texas, the following officers for 1923 were elected: N. C. Hammer, chairman; W. Arthur, vice chairman; W. W. Battle, secretary-treasurer; J. R. Bailey, councilor. W. W. Battle, Secretary

### CHICAGO SECTION

On January 19, the program of the meeting was under the auspices of the women members of the Section, Miss Elizabeth Weirick presiding. The address of the evening was by Mrs. Elizabeth Miller Koch on "Sunlight as a Factor in the Vitamin Problem." Group meetings with discussions of subjects under (1) laboratory methods (inorganic), (2) laboratory methods (inorganic), (3) synthetic, and (4) biologic, were conducted.

S. L. Redman, Secretary

# CINCINNATI SECTION

The 255th regular meeting of the Section was held on January 17, and was addressed by Carey Pratt McCord, and Robert A. Kehoe, both of the University of Cincinnati, their subjects being "Some Aspects of Industrial Poisoning," and "The Nature of Heavy Metal Poisoning and its Relief," respectively.

The following officers for the Section have been elected for 1923: Martin H. Fischer, president; A. S. Richardson, vice president; H. M. Williams, second vice president; A. O. Snoddy, secretary-treasurer; Archibald Campbell, trustee; C. P. Long, A. B. Davis and H. J. Morrison, councilors.

A. O. Snoddy, Secretary

### CLEVELAND SECTION

At the regular meeting of the Section, held on December 27, George Oenslager, of the B. F. Goodrich Rubber Co., addressed the members on "The Rubber Plantation Industry in the Far East and the Preparation of Rubber for the World's Market." At this meeting the following officers for 1923 were elected: W. R. Veazey, chairman; L. C. Drefahl, vice chairman; H. S. Booth, secretary-treasurer; L. C. Drefahl, A. W. Smith, O. F. Tower and W. R. Veazey, councilors.

The members of the Section were invited to attend the meeting of the Associated Technical Societies of Cleveland on the night of January 9, the topic of the evening's addresses being "The Steel Industry as Affected by the Life of the late Samuel T. Wellman."

H. S. BOOTH, Secretary

# CONNECTICUT VALLEY SECTION

On January 13, the members of the Section enjoyed a trip through the Strathmore Paper Company's plant at Springfield, Mass. In the evening of that day, an address was given by William P. Ryan, of the Massachusetts Institute of Technology on "Some Aspects of the Sizing of Paper."

PAUL SERREX, JR., Secretary

# CORNELL SECTION

At a meeting of the executive council of the Section, held on December 14, A. W. Browne was elected to serve as councilor.

F. E. Hance, Secretary

### DELAWARE SECTION

At the December 20th meeting, the following officers for 1923 were elected: F. C. Zeisberg, chairman; J. F. Garrett, vice chairman; J. L. Bennett, treasurer; J. W. Stillman, secretary; C. L. Reese and C. M. Stine, councilors.

J. W. STILLMAN, Secretary

#### DETROIT SECTION

The regular meeting of the Section was held on January 17, when William K. Sawyer, of Morgan & Wright Company, Detroit, Mich., spoke on the subject, "Cotton Fabrics."

S. R. Wilson, Secretary

### EASTERN NEW YORK SECTION

The following officers for 1923 have been elected: G. R. Fonda, chairman; Arthur Knudson, vice chairman; Edward Darby, secretary-treasurer; Saul Dushman and Edward Ellery, councilors; G. M. J. Mackay, Mrs. M. R. Andrews and W. P. Davey, executive committee.

E. H. DARBY, Secretary

### INDIANA SECTION

On December 8, the members of the Indiana Section were the guests of the Van Camp Packing Co., at Indianapolis. A complimentary dinner was served to the 135 guests present. The trip of inspection was preceded by a talk by Mr. Rutledge of the Van Camp Company who welcomed the guests and explained some of the plant operations. Two talks followed the trip, one by C. E. Stone on "Progress of Science in Food Preservation, and one by W. L. Clark, on "The Manufacture and Analysis of Evaporated Milk."

E. R. Weidlin, director of the Mellon Institute of Industrial Research, addressed the Section, on January 12, his subject being "The Value of Industrial Research."

WILLIAM HIGBURG, Secretary

### IOWA SECTION

The regular monthly meeting of the Section was held at Iowa City on December 13, with the following program: "The Promoter Action of Certain Compounds on the Activity of Urease," by W. J. Husa; "The Weight of the Acyl Radical as a Factor in the Molecular Rearrangement of Diacylated Ortho-Aminophenols," by J. R. Couture; and "The Effect of Acidity of the Radical in the Molecular Rearrangement of Diacylated Ortho-Aminophenols."

On January 12, Victor Lenher, of the University of Wisconsin, lectured before the Section, his subject being "Selenium Oxychloride."

The following officers for 1923 have been elected: L. Chas. Raiford, chairman; H. F. Lewis, vice chairman; G. H. Coleman, secretary; Edward Bartow, councilor.

G. H. COLEMAN, Secretary

# KANSAS CITY SECTION

On December 16, H. P. Cady gave an address before the members, his subject being "The Composition of the Atom." At this meeting the following officers for 1923 were elected: R. Q. Brewster, chairman; C. F. Gustafson, vice chairman; Lee E. Clark, secretary-treasurer; Robert Taft, assistant secretary; F. B. Dains and Rudolph Hirsch, councilors.

At the meeting of the Section, held on January 17, Wm. J. Reese spoke on "The Interpretation of the Analysis of Soap Materials."

Lee E. Clark, Secretary

### LEHIGH VALLEY SECTION

The following officers have been elected by the Section for 1923: E. C. Bingham, chairman; L. F. Witmer, vice chairman; R. H. Bogue, secretary-treasurer; J. P. Little, councilor.

R. H. Bogue, Secretary

### LOUISVILLE SECTION

At the November meeting of the Section, the following officers for 1923 were elected: C. E. Bales, chairman; T. J. Bosman, vice chairman; C. E. Geiger, secretary-treasurer; A. W. Homberger, councilor; T. J. Bosman, R. Camp and C. E. Geiger, membership committee; C. E. Bales, A. W. Homberger and G. A. Goodell, program committee.

C. E. GEIGER, Secretary

### MAINE SECTION

At the regular meeting of the Section, held on January 12, C. A. Brautlecht, of the University of Maine, addressed the members on the subject, "Chemistry of Fuel, Heat and Light (Illustrated)."

The following officers have been elected by the Section for 1923: C. A. Brautlecht, president; J. M. Bartlett, vice president; N. E. Woldman, secretary-treasurer; A. B. Larchar, councilor.

N. E. Woldman, Secretary

# MARYLAND SECTION

The 61st meeting of the Section was held on December 29, with the following program: "Trivalent Titanium in Analysis," by W. M. Thornton; "Soil Colloids and the Theory of Adsorption," by Neil Gordon; and "A Laboratory-made Vacuum Oven," by W. B. D. Penniman.

ADOLPH HARVITT, Secretary

### MIDLAND SECTION

The 14th meeting of the Section was held on November 21, when M. E. Putman discussed the New York Chemical Exposition, and Ralph Hunter spoke on "Electrolytic Caustic Cells."

The 15th meeting occurred on December 19. Roy Osmun presented a paper on the "Transformations, Uses, Losses, and Costs of the Heat Energy of Coal in the Dow Chemical Plants."

John A. Gann, Secretary

# MILWAUKEE SECTION

On January 12, C. A. Nash addressed the members of the Section on the subject, "The Chemist in the Molding Industry."

A. A. CHAMBERS, Secretary

# NEW HAVEN SECTION

At the regular meeting of the Section, held on January 16, R. E. Swain, of Leland Stanford University, spoke on "Some Aspects of the Smoke Problem."

BLAIR SAXTON, Secretary

# NEW YORK SECTION

A joint meeting of the local Section and the Societe de Chimie Industrielle was held on January 5. A special program was arranged commemorating the centenary of the birth of Louis Pasteur, as follows: "Pasteur and the Science of Fermentation," by Gary N. Calkins, of Columbia University; "Pasteur and Chemical Asymmetry," by John M. Nelson, of Columbia University. John W. Churchman, of Cornell University, spoke on "The Selective Bacteriostatic Properties of Certain Dyes."

The following officers for 1923 have been elected by the Section: C. A. Browne, chairman; C. E. Davis, vice chairman; B. T. Brooks, secretary-treasurer; Martin H. Ittner, James Kendall, H. C. Parmelee, and Herbert G. Sidebottom, executive com-

mittee; C. A. Browne, C. E. Davis, B. T. Brooks, James Kendall, H. C. Parmelee, H. G. Sidebottom, R. G. Wright, T. H. Getmann, Ellwood Hendrick, K. G. MacKenzie, David Wesson, H. R. Moody, Martin H. Ittner, A. C. Langmuir, D. W. Jayne, B. R. Tunison, A. W. Thomas, W. Haynes, and Lois M. Woodford, councilors.

B. T. BROOKS, Secretary

### NORTHEASTERN SECTION

The 181st meeting of the Section occurred on January 12. George B. Magrath, medical examiner of the Suffolk District, spoke on "Medical Examiner Service." Motion pictures showing the operations of the American Sugar Refining Company were shown and explained by W. van V. Warren.

E. B. Millard, Secretary

### PHILADELPHIA SECTION

On January 18, Julius Stieglitz, of the University of Chicago, addressed the members of the Section, his subject being "Some Problems in the Field of Chemistry and Medicine."

J. HOWARD GRAHAM, Secretary

# PITTSBURGH SECTION

The 184th meeting of the Section was held on January 18, with the following program: "Manufacture and Use of Enamel-Lined Apparatus," by Emerson P. Poste; "Manufacture and Properties of Oven Glass Cooking Ware," by Ralph F. Brenner; and "Manufacture of Electrical Porcelain," by E. H. Fritz.

The following officers have been elected by the Section for 1923: E. R. Weidlein, chairman; A. Silvermann, vice chairman; E. S. Stateler, secretary; C. E. Nesbitt, treasurer; A. C. Fieldner, J. O. Handy, E. W. Tillotson, R. E. Zimmerman, and H. C. P. Weber, councilors.

### PUGET SOUND SECTION

The Section has elected the following officers for 1923: Thomas G. Thompson, chairman; A. G. Bissell, vice chairman; R. W. Ellison, secretary; G. C. Howard, treasurer; H. K. Benson, councilor.

R. W. Ellison, Secretary

# PURDUE SECTION

The regular monthly meeting of the Section was held on December 14, when R. H. Carr, of Purdue University, gave a lecture on "Soil Toxicity," and F. O. Anderegg, of Purdue University, on "Water, The Most Peculiar Liquid."

MARGUERITE G. MALLON, Secretary

# ROCHESTER SECTION

The 147th regular meeting of the Section was held on January 8, when C. E. K. Mees spoke on "Motion Picture Photography for the Amateur."

On January 19 and 20, the Section presented a symposium on Physical Chemistry, with seventeen speakers giving lectures on that subject. Erle M. Billings, Secretary

# SACRAMENTO SECTION

At the meeting of the Section, held on January 13, G. H. P. Lichthardt, of the California State Department of Public Works, spoke on "Colloidal Chemistry and Its Application."

J. H. Norton, Secretary

### SAINT LOUIS SECTION

On January 8, the Section had the following program: "Beyond the Microscope," by Gerald L. Wendt.

H. A. Carlton, Secretary

### SOUTHEAST TEXAS SECTION

The following officers have been elected by the Section for 1923: L. S. Bushnell, president; W. A. Slater, vice president; L. B. Howell, treasurer; P. S. Tilson, secretary; F. M. Seibert, councilor.

P. S. Tilson, Secretary

# SOUTH JERSEY SECTION

The 17th regular meeting of the Section occurred on December 12, the following papers being presented: "Vitamins from a Historical and Chemical Standpoint," by W. S. Calcott; and "Vitamins from a Medical Standpoint," by R. S. Sutherland.

On January 24, W. A. Peters, Jr., addressed the members of the Section, his subject being "Recent Developments in the Theory and Practice of Distillation."

The following officers for 1923 have been elected: H. W. Mahr, chairman; A. F. Odell, vice chairman; W. Fletcher Twombly, secretary-treasurer; W. S. Calcott, councilor.

W. FLETCHER TWOMBLY, Secretary

### SYRACUSE SECTION

On January 3, R. Adams Dutcher, of Pennsylvania State College, addressed a special meeting of the Section, his subject being "Vitamins."

At the regular meeting of the Section, held on January 12, G. I. Vincent addressed the members on the subject, "The Manufacture of Gas."

M. T. Bogert, of Columbia University, gave a lecture before the members of the Section on January 26. His subject was "Perfumes, Natural and Synthetic."

W. B. HICKS, Secretary

#### TOLEDO SECTION

At the regular meeting of the Section, held on December 19, Carrol S. Lyman spoke on "The Manufacture of Asphalt Blocks."

On January 8, Robert E. Wilson, of the Standard Oil Company, addressed the Section, his subject being "The Mechanism of the Corrosion of Iron."

GUY E. VAN SICKLE, Secretary

# UNIVERSITY OF ILLINOIS SECTION

The regular meeting of the Section was held on December 20. F. W. Mohlman, chief chemist for the Sanitary District of Chicago, spoke on "Chicago's Sewage Disposal problems."

The 126th regular meeting of the Section occurred on January 12, when F. C. Whitmore, of Northwestern University, addressed the members on the subject "The Human Side of Mercury."

D. T. Englis, Secretary

# UNIVERSITY OF MICHIGAN SECTION

The annual business meeting of the Section was held on December 14, when the following officers for 1923 were elected: C. S. Schoepfle, chairman; H. H. Willard, councilor; C. C. Meloche, secretary; W. L. Badger, A. L. Ferguson and R. K. McAlpine, executive committee.

On January 16, A. H. White spoke before the Section on the subject, "Waterproof Concrete."

C. C. Meloche, Secretary

# UNIVERSITY OF MISSOURI SECTION

On December 7, W. N. Stull, of the Mallinckrodt Chemical Works, St. Louis, Mo., spoke before the meeting of the Section, his subject being "Qualifications Necessary in an Industrial Chemist."

The following officers for 1923 have been elected: H. Schlundt, chairman; I. Stanley, vice chairman; H. D. Hooker, Jr., councilor; H. E. French, secretary; and M. V. Dover, treasurer.

H. E. French, Secretary

# Proceedings

# ADVISORY COMMITTEE

On February 3, 1923, the following communication was sent to the Committee on National Policy, and was unanimously approved:

Washington, D. C., February 3, 1923

Committee on National Policy, American Chemical Society: Gentlemen:

The enclosed documents which the Chairman of our Committee on Industrial Alcohol wishes me to send you for your approval are self-explanatory. The Secretary has no additional information except to state that, so far as he is aware, it is the unanimous opinion of all those who have looked into the matter that the proper administration of Title 3 and the appointment of a special industrial alcohol commissioner will unquestionably add both to prohibition enforcement and to the proper use of alcohol for industrial purposes. The chairman of the committee writes me that they have taken the matter up informally with some of the leading officers of the Government and that they have good reasons to believe that these arguments will be welcome and appropriate.

Will you kindly send in your approval or disapproval at the earliest possible moment.

Sincerely yours,

CHARLES L. PARSONS
Secretary

The American Chemical Society recognizing the necessity for proper legal provision for a supply of alcohol, and for the use of alcohol as a chemical raw material and for other lawful purposes, on the advice of its Committee on Industrial Alcohol regularly established for the purpose of consulting and advising on matters pertaining to industrial alcohol, as a whole through its Committee on National Policy hereby presents the following recommendation:

"In order that the National Prohibition Act may be more equitably and effectively administered and that industries depending upon the use of industrial alcohol may be permitted to operate under reasonable regulations and be encouraged as expressly provided in the law, and in order that violations of the law may be more readily prosecuted, the American Chemical Society recommends that Title 3 of that act pertaining to industrial alcohol shall be given equal weight in enforcement with other portions of the act, and recommends that, to this end an Industrial Alcohol Commissioner be appointed with authority equal to an apart from the Prohibition Commissioner, whose duties shall be the administration of those portions of the law pertaining to industrial alcohol."

The enforcement of the National Prohibition Act has been, up to the present, largely in the hands of the Prohibition Commissioner. This officer has naturally been selected principally because of his fitness to enforce the prohibition features of the law. It is perhaps too much to expect that the Prohibition Commissioner shall be a technical man and that he shall in addition to his policing duties in the interest of prohibition also jealously guard the interests of alcohol-using industries, yet this is precisely what the law contemplated as evidenced by section 13 Title 3 of the National Prohibition Act which is as follows:

"The Commissioner shall from time to time issue regulations respecting the establishment, bonding, and operation of industrial alcohol plants, denaturing plants, and bonded warehouses authorized herein, and the distribution, sale, export, and use of alcohol which may be necessary, advisable, or proper, to secure the revenue, to prevent diversion of the alcohol to illegal uses, and to place the non-beverage alcohol industry and other industries using such alcohol as a chemical raw material or for other lawful purpose upon the highest possible plane of scientific and commercial efficiency consistent with the interests of the Government, and which shall insure an ample supply of such alcohol and promote its use in scientific research and the development of fuels, dyes, and other lawful products."

The Commissioner is specifically charged in this section with broad and important duties of administration. We recommend that the Commissioner, acting on the authority here conferred, apportion the administration of the law among the coördinated officers, both holding office as Assistant Commissioners of Internal Revenue; the Industrial Alcohol Commissioner, and the Prohibition Commissioner.

With an Industrial Alcohol Commissioner, preferably a technical man himself, and with technical men on his staff, the needs of the industries would necessarily be better looked after and it would be easier thus to prevent diversions of alcohol to unlawful purposes, such as have occurred in the past where the granting of permits has been left to men unfamiliar with the industries but selected mainly because of their fitness to enforce the prohibition end of the law.

With two coordinated officers looking after industrial alcohol and prohibition enforcement, the possibility of unlawful procurement of alcohol through corruption would be greatly lessened.

MARTIN H. ITTNER.

Chairman, Committee on Industrial Alcohol, American Chemical Society

# **AUDITORS' REPORT**

New York, Tanuary 18, 1923

Dr. J. E. Teeple, Chairman Finance Committee:

American Chemical Society

50 East 41st Street, New York City

### Dear Sir:

Pursuant to your request, we have made an audit of the books of account of the American Chemical Society, kept by its Treasurer, for the year ending December 31, 1922, and submit herewith the accompanying Condensed General Balance Sheet as of December 31, 1922, and Statement of Cash Received and Disbursed Between January 1, and December 31, 1922—marked Exhibit "A" and Exhibit "B," respectively, which we have prepared thereform; and hereby

CERTIFY that such statements correctly reflect the financial condition of the Society at December 31, 1922 and its financial transactions during the year, as shown by the books of account.

# Yours very truly,

(Signed) McCulloh and Brown
Certified Public Accountants

# AMERICAN CHEMICAL SOCIETY

Condensed General Balance Sheet—December 31, 1922

### ASSETS

### INVESTMENTS:

Special Investment Fund:	
\$ 1,000 Brooklyn Rapid Transit 7% Notes.	\$ 1,000.00
1,000 Hocking Valley Railway 1st Mort-	
gage $4^{1}/_{2}\%$ , Due July 1, 1999	1,000.00
6,000 Illinois Central—Chicago, St. Louis	
and New Orleans—Joint Refund-	
ing 5% Mortgage, Due December	
1, 1963	6,000.00
1,000 New York Connecting Railway 1st	
Mortgage 41/2%, Due August 1,	
1953	1,000.00
2,000 Atlas Portland Cement 6%, Due	
March 1, 1925	2,000.00
2,000 Corporate Stock, City of New York	
4 ¹ / ₂ %, Due June 1, 1965	2,000.00
5,000 New York Central Refunding & Im-	
provement 41/2% Series "A,"	
Due October 1, 2013	5,000.00
10,000 United States Steel Corporation	
5%, Due April 1, 1963	10,000.00

15,000 United States Liberty 2nd $4^{1}/_{4}\%$ ,			
Due 1942	14,608.00		
20,000 United States Liberty 3rd 41/4%,	10 100 00		
Due 1928	19,400.00		
Due 1933–1938	14,604.00		
10,000 New York Telephone Company $6\%$ ,	•		
Due February 1, 1949	9,987.50		-
10,000 United Kingdom of Great Britain and Ireland 5½%, Due February			
1, 1937	9,875.00		
10 Shares Chemical Foundation Inc., Stock			
—(Subscription Receipt Central	1.000.00		
Union Trust Company)	1,000.00		•
Total		\$97,474.50	
Life Membership Fund:			
\$ 1,000 United States Liberty 2nd 41/4%,	# 000 ME		
Due 1942	\$ 906.75		
Due 1933–1938	906.95		
1,000 Corporate Stock, City of New York	1 000 00		
$3^{1}/_{2}\%$ , Due November 1, 1928 2,000 Mutual Union Telegraph 5%, Due	1,000.00		
May 1, 1941	2,000.00		
Total	1	4,813.70	
Morris Loeb Fund:		1,010.7	
\$ 5,500 United States Liberty 1st 41/4%.			
Due 1932–1947	\$ 4,804.90		
6,000 United States Liberty 4th 41/4%,	# 400 00		
Due 1933–1938	5,100.90		
gage $4^1/2\%$ , Due July 1, 1999	5,000.00		
5,000 Illinois Central—Chicago, St. Louis			
and New Orleans—Joint 1st Mortgage Refunding 5%, Due			
December 1, 1963	5,000.00		
5,000 New York Connecting Railway 1st			
Mortgage, Due August 1, 1953	5,000.00		
Total		24,905.80	
Priestley Memorial Fund:			
\$ 200 Federal Farm Land Bank 5%			
Bonds	\$ 205.71		
800 United States Liberty 4th 4 ¹ / ₄ %, Due 1933–1938	789.70		
100 United States Victory 43/4%, Due			
1923	102.07		
Total	Parting Tolky	1,097.48	

Total Investments.  Office Furniture and Fixtures.  Publications—(Extra Copies Held for Future Sales).  Current Assets:	\$128,291.48 4,772.71 8,000.00
Cash on Hand—as per Exhibit "B"       \$ 4,844.67         Accounts Receivable—Advertising       15,100.27	
Total	19,944.94
Total Assets	\$161,009.13
American Chemical Society Condensed General Balance Sheet, Etc.	And the second s
Liabilities	
Trust Funds and Unexpected Cash Balances:	
Life Membership Fund. \$ 5,411.55 Life Membership Fund Income—Dues and Interest. 264.52 Morris Loeb Fund. 25,100.90 Priestley Memorial Fund. 1,157.91	
Priestley Memorial Fund Income	
Total  BALANCE—BEING EXCESS OF ASSETS OVER LIABILITIES	\$ 31,943.68 129,065.45
Total Liabilities	\$161,009.13
American Chemical Society, kept by its Treasurer, and have prepared to foregoing Balance Sheet, which correctly reflects the financial condition of as at December 31, 1922, as shown by its books of account.  The Cash in Bank was proven by certificate from the depositary, curities shown as constituting the Investment of General and Trust Funds \$128,291.48, are in accord with the certified list furnished by the Treasurer of The verification of these Securities is not now possible, owing to the alternature, who is abroad.  (Signed) McCullon & Brown	of the Society while the Se- , aggregating of the Society.
Certified Public Accountants	•
American Chemical Society	
Statement of Cash Received and Disbursed between January December 31, 1922 Receipts	1, AND
	JI.
Cash on Hand January 1, 1922  Dues and Subscriptions:  Membership Dues and Subscriptions	
Miscellaneous:	2.0,007.100
Notes Payable—Discounted	
ing Interest Realized Therefrom	
Priestley Memorial Trust Fund Committee 850.13 Monograph Royalties 256.64	

Chemical Foundation—For Restoration of Impaired Surplus.	5,000,00	
pius	5,000.00	
Total		76,106.77
Revenue from Publications:		
Advertising	\$89,039.11	
Non-Members Subscriptions	21,292.48	
Back Numbers	6,139.44	
Directories	28.50	
Reprints (Secretary's Office)	3,739.10	
Total		120,238.63
Decennial Index:		
Subscriptions and Contributions		565.00
Income from Investments, Etc.:		
Special Investment Fund	\$ 5,075.00	
Temporary Investments	365.56	
Life Membership Fund	220.00	
Morris Loeb Fund	1,188.75	
Priestley Memorial Fund	8.80	
General Funds—Interest on Bank Balances	1,550.08	
Total		8,408.19
Prepayment of Expenses, Etc.:		
Payments by Members for Postage	\$ 4 226 25	
Miscellaneous Items	. ,	
Total		4,227.16
Total Receipts		\$385,144.24
		φοσο, 111121
DISBURSEMENTS		
INVESTMENTS AND CAPITAL EXPENDITURES:	2.3	
Securities Purchased:		
Unites States Liberty Bonds 4th $4^{1}/_{4}$ (Priestley		
Memorial Fund)		
Temporary Investments	10,050.00	
Total		\$ 10,839.70
Temporary Loans—Notes Discounted Paid		25,000.00
Interest Payment to Smithsonian Institute from M	orris Loeb	
Fund Income		1,188.75
Publication Expenses:		
Journal:		
Editor's Salary \$ 1,500.00		
Clerical Salaries		
Expenses		
Printing Reading Matter 40,346.60		
Printing Reprints		
\$47,10U.10		일하면 왜 없다.

Chemical Abstracts:	
Editor's Salary \$ 4,500.00	
Assistant Editors' Salaries 4,550.00	
Abstractors 12,041.73	
Clerical Salaries 5,785.38	
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· manage and a second control of the	
	15
98,965	.10
Journal of Industrial and Engineering Chemistry:	
Editor's Salary \$10,000.00	
Assistant Editor's Salary 2,800.00	
Associate Editor's Salary 2,510.00	
Staff Correspondents	
Clerical	
Expenses	
Office Rent	
Printing Reading Matter 36,157.75	
Printing Reprints 3,361.78	
70,084	.58
A #	· ·
Advertisements:	
Printing, Reprints, Cuts, etc.—General 30,955	.91
News Service:	
Technical Manager \$ 4,500.00	
Clerical Salaries	
Office Rent	
Expenses	
10,653	.82
Back Numbers	.21
#PROGRAMMENT AND ADDRESS OF THE PROGRAMMENT AND ADDRESS OF THE	
Total	
Local Sections	8,588.86
Forward	#907 A02 10
PORWARD	\$305,026.13
Secretary's Office:	
Secretary's Salary	\$ 5,000.00
Clerical Salaries	10,441.00
Office Rent—Net	
Expenses	
	Charles and the contract of th
Total	
Treasurer's Office:	
Treasurer's Salary	¢ 1,000,00
Clerical Salaries	
Expenses	920.87
Total	3,360.87
President's Office—Expenses.	
Expenditures for 1921 from 1922 Receipts	
The state of the s	20,000.00

General Expenses:		
General Meetings	\$ 1.762.41	
International Tables of Physical and Chemical Constants Monographs:		
Editor's Salaries \$ 2,000.00		
Expenses		
	2,065.50	
Interest on Borrowed Capital	118.75	
Metric System Committee		
Incidentals	492.86	
Total		4,980.67
Total Disbursements	• • • • • • • • • •	\$360,173.58
Add:		
Excess of Amounts Recorded as Disbursed During the Yea	ar 1921 over	
the Amount on Deposit with the Farmers Loan & Tru		
during the same period; such Excess Disbursed Represen	iting certain	
bills for Printing, etc., payment of which, however, w	vas made in	
January 1922		20,125.99
Total		\$380.200.57
Balance—Cash on Hand December 31, 1922.		4,844.67
GRAND TOTAL		\$385.144.24

# COUNCIL

# MEMBERS ELECTED BETWEEN JANUARY 15, AND FEBRUARY 15, 1923

Abson, Gene, 160 N. Wells, Chicago, Ill. Adams, Harry M., Earle Chemical Co., Wheeling, W. Va. Anderson, Edla V., 1558 Fulham St., St. Paul, Minn. Arthur, Edwin P., 8 University Place, Columbus, Ohio. Atwater, Arthur C., 45 Barclay St., Canajoharie, N. Y. Austin, J. Bliss, Section A., Taylor Hall, Lehigh University, Bethlehem, Pa. Baborovsky, Dr. George, Falkensteinerova 7, Brno, Czechoslovakia. Baxter, Warren P., 981 East Villa St., Pasadena, Cal. Beard, Harold C., Carnegie Institute of Tech., Pittsburgh, Pa. Beiswenger, Gustav A., 1533 Commonwealth Ave., New York City. Berg, Orville M., Phi Beta Psi House, Gainesville, Florida. Beschenbossel, Walter, Carnegie Tech., Pittsburgh, Pa. Bixby, Louis E., McPherson, Kans. Blackford, H. L., 180 St. James St., Montreal, Canada. Boutelle, Bertha, 138 Montvale Ave., Woburn, Mass. Brenner, Harold M., 250 Bellefield Ave., Pittsburgh, Pa. Brierley, John Thomas, Highfield, Leyland, near Preston, England. Brown, Harry Silsby, 1355 Benton, Springfield, Mo. Brunner, E. Max, 546 University Ave., Chicago, Ill. Buckner, H. K., 6234 Ellis Ave., Chicago, Ill. Burd, Lillian A., Goucher College, Baltimore, Md. Burks, Harry G., Jr., 44 The Fenway, Boston, Mass. Burns, James W., 306 King St., London, Ont., Canada. Caldwell, C., T., 109 S. Babcock St., Urbana, Ill. Camp, Lee Gordon, Obrapia No. 19, Box 1973, Habana, Cuba. Campbell, Marion S., 29 N. Hawthorne Lane, Indianapolis, Ind. Carson, C. M., 395 Mell Ave., Akron, Ohio. Cheek, Dorothy Louise, 19 Greene St., Pawtucket, R. I.

Cheever, Telford C., Montpelier, Vermont.

Chiao, C, L., Council Hall, Oberlin, Ohio.

Child, Alice M., 2256 Carter Ave., St. Paul, Minn.

Childs, Wesley H., 130 Dryden Road, Ithaca, N. Y.

Chuji, Fujioka, Imperial Industrial Laboratory, Hatagaya, Tokyo, Japan.

Churchman, John Woolman, 45 East 55th St., New York City.

Clark, Olive E., Colton, Cal.

Cochran, P. B., 1312 Elm St., Wilkinsburg, Pa.

Colin, G. G., Box 213, Lake Bluff, Illinois.

Cook, E. C., Thaw Building, 108 Smitfield St., Pittsburgh, Pa.

Cook, Warren A., Epsilon Kappa Phi House, Hanover, N. H.

Cori, Karl F., 368 Bryant St., Buffalo, N. Y.

Courtney, R. P., 417 Waldron, W. Lafayette, Indiana.

Cox. Morgan Butler, 1930 Tamarind Ave., Los Angeles, Cal.

Crago, Arthur, Copperhill, Tenn. (Tennessee Copper Co.).

Cunningham, Henry, 18612 Shawnee Ave., Cleveland, Ohio.

Dallahan, Hugh A., 604 E. Springfield Ave., Champaign, Ill.

Dargie, Andrew, 140 Perth Road, Dundee, Scotland.

Davenport, Bertram, Calico Printers' Assoc., Ltd., St. James Bldgs., Manchester, England.

Davis, George Francis, Davis Gelatine (Australia), Ltd., 4 Bridge St., Sydney, New South Wales, Australia.

Dempsey, A. Evelyn, Belleville, Ont., Canada.

Denham, William Smith, British Silk Research Association, University, Leeds, England.

Denise, Sister M., Notre Dame College, Charles Str. Ave., Baltimore, Md.

Desy, G. G., Mellon Institute, Pittsburgh, Pa.

Diamond, Grant S., 888 Michigan Ave., Buffalo, N. Y.

Dick, John B., U. S. Finishing Co., Norwich, Conn.

Eglof, Warren K., 361 Ninth St., Troy, N. Y.

Ellis, Oliver Coligny de Champfleur, 12 Avondale Road, Hillsborough, Sheffield, England.

Farmer, Max D., 41 Park Row, New York City.

Fichandler, 704 E. Buffalo St., Ithaca, N. Y.

Fleming, Walter E., Box 69, Riverton, N. J.

Fogle, Ralph W., 61 E. Springfield, Champaign, Ill.

Fong, Thomas S., City Y. M. C. A., Madison, Wis.

Foulke, John Louis, 1208 W. Cambria St., Philadelphia, Pa.

Frear, George Lewis, 246 Pugh St., State College, Pa.

Freer, Richard M., 23 Converse Hall, Burlington, Vt.

Fullen, W. J., Geo. A. Harmel & Co., Austin, Minn.

Garber, John T., 407 East Liberty St., Ann Arbor, Mich.

Garbrecht, Charles, P. O. Box 581, Freeport, Texas.

Garey, Luther T., 907 S. 6th St., Champaign, Ill.

Giauque, W. F., Gilman Hall, University of California, Berkeley, Cal.

Cilbert, T. M., 224 Ash Ave., Ames, Iowa.

Glover, Clifford C., 611 Hoover Ave., Ann Arbor, Mich.

Gonser, B. W., 417 Waldron St., W. Lafayette, Indiana.

Gould, Edward, 2135 Ave D., Carney's Point, N. J.

Gray, L. T. M., Italian House, Meadow Green, Welwyn Garden City, Herts, England

Gregory, Brother, 1416 North Meridian St., Indianapolis, Indiana.

Guerin, Frederick J., 127 Butler St., Lawrence, Mass.

Gurchot, Charles, 409 Dryden Road, Ithaca, N. Y.

Guyer, Paul B., 130 Comrie Ave., Braddock, Pa.

Haas, Joseph L., 20 Alexander St., Framingham, Mass.

Hagarty, John J., 3710 Ave I., Brooklyn, N. Y.

Hall, Albert, 583 Leonard St., Brooklyn, N. Y.

Harris, John McArthur, Jr., 105 Walnut Lane, Germantown, Philadelphia, Pa.

Hauser, Chas. Roy, Box 55, University Station, Gainesville, Florida.

Haworth, Ellis, 132 Thirteenth St., S. E., Washington, D. C.

Heastan, Elmer J., 139 Bausman St., Pittsburgh, Pa.

Hendrickson, Edwin H., 720 E. Clark St., Vermillion, S. Dak.

Henninger, Arthur H., 90 North 17th St., Flushing, New York City.

Henriques, H. J., 2231 Dana St., Berkeley, Cal.

Himmel, Mildred, 2201 Callow Ave., Baltimore, Md.

Hoffman, R. Vincent, 307 Cascadilla Hall, Ithaca, N. Y.

Hooker, Lorren G., 817 East State St., Ithaca, N. Y.

Hopper, Turner H., Agricultural College, North Dakota.

Hunt, Galen, Box 194, Station A, Ames, Iowa.

Hutchinson, Alfred, Manesty, Saltburn-by-the Sea, Yorkshire, England.

Iseki, N., 309 W. 111th St., New York City.

Jameson, Archibald Y., 1456 Orange Grove Ave., Hollywood, Los Angeles, Cal.

Jameson, Henry John, 1415 23rd St., Detroit, Michigan.

Jarrett, Guy M., Sylvania, Ohio.

Jenkins, Francis A., 5411 Greenwood Ave., Chicago, Ill.

Jewett, Eugene Lyon, 620 Thurston Ave., Ithaca, N. Y.

Johnson, Alam C., 601 Clay St., Topeka, Kans.

Johnson, Clifford S., 11236 Watt Ave., Chicago, Ill.

Johnson, Irvin, 868 Buffum St., Milwaukee, Wis.

Jones, Irwin Harvey, Mellon Institute, Pittsburgh, Pa.

Kadeson, Sara Ruth, 4537 Drexel Blvd., Chicago, Ill.

Kelso, John W., 315 Euclid Ave., Drovosburg, Pa.

Kerns, Proctor M., 1432 Diamond St., Philadelphia, Pa.

Kessler, Emil H., 57 Findlay St., South, Dayton, Ohio.

Kessler, Otto, Jr., 233 W. Wyoming St., Gtn., Philadelphia, Pa.

Kirk, Paul L., 212 W. 10th Ave., Columbus, Ohio.

Klein, Leroy N., 707 S. Gregory St., Urbana, Ill.

Kohlerman, James H., 1305 West Third St., Wilmington, Del.

Koppitz, Carl G., 437 N. Maple Ave., Greensburg, Pa.

Krasnow, Frances, 437 W. 59th St., New York City.

Kresse, Alfred R., 1121 Bedford Ave., Brooklyn, N. Y.

Kurihara, Kozaburo, 56 Obancho, Yotsuyaku, Tokyo, Japan.

Labarthe, Jules 3620 Terrace St., Pittsburgh, Pa.

Latrobe, Charles H., 17, Cleveland Ave., Buffalo, N. Y.

Lawson, J. H. S. c/o R. P. Lawson & Sons, Ltd., Rodney St., Oldham Road, Manchester, England.

Leadbetter, Harold Duff, Salcombe Graham Road, Purley, Surrey, England.

Leighou, Robert Benjamin, Carnegie Institute of Tech., Pittsburgh, Pa.

Lilliendahl, William C., 373 Ocean Ave., Brooklyn, N. Y.

Lotz, Paul L., 14 Tenth St., Long Island City, N. Y.

Mann, Raymond F., 292 Fairmount Ave., Hyde Park, Mass.

Markowski, Mitchell, 1632 Church St., Detroit, Mich.

Mason, Clyde Walter, Morse Hall, Cornell University, Ithaca, N. Y.

Mason, John Philip, 52 Graduate College, Princeton, N. J.

Maude, A. H., Research Dept., Westinghouse Electric & Mfg. Co., E. Pittsburgh, Pa.

Maxwell, Harry Buddington, 329 W. Dominick St., Rome, N. Y.

McConnell, Elliott B., 600 University Ave., Ithaca, N. Y.

McKinney, Paul V., 319 W. Wayne St., Celina, Ohio.

McLaren, Donald W., 4205 So. 23rd St., Omaha, Neb.

McLoughlin, Henry W., Loyola College, Calvert and Madison Sts., Baltimore, Md.

Miller, Milton M., 1404 Raymond Ave., St. Paul, Minn.

Mills, William Hobson, The Red House, Chesterton Road, Cambridge, Eng.

Mitchell, Allan Ernest, Physico-Chemical Lab., University College, Gower St., London, England.

Monson, Harold H., 107 Kansas City St., Rapid City, S. Dak.

Moore, Catherine M., 234 Oakland Ave., Pittsburgh, Pa.

Morgan, Russell, 716 South Fourth St., Clinton, Iowa.

Morse, Rowena A., Greentrees, Ithaca, N. Y.

Nadeau, Herve, 932 Rue St. Denis, Montreal, Canada.

Nixon, L. M., Dept. of Agriculture, Raleigh, N. Car.

O'Donovan, James L., 13 Grace Park Gardens, Dublin, Ireland.

Oke, Ernest, 304 Durie St., Toronto, Ont., Canada.

Olson, Charles B., 824 6th St., Rapid City, S. Dak.

Perkins, Maurice, 124 St. Awdrys Road, Barking, Essex, England.

Pfaltz, Mimosa Hortense, 490 Riverside Drive, New York City.

Potter, Elbert L., Jr., 1212 E. University Ave., Ann Arbor, Mich.

Prisley, Frederic A., 380 Pearl St., Burlington, Vt.

Rees, Orin W., Earlham College, Richmond, Indiana.

Reese, Earle F., 332 South Fifth, Darby, Pa.

Reuber, Joseph M., 2056 E. 107th St., Cleveland, Ohio.

Rollhaus, P. Edward, 354 Quincy St., Brooklyn, N. Y.

Rubach, Stephen, 47 Gates Ave., Sloan, N. Y.

Rummel, Olga F., 2131 Sinton Ave., W. H., Cincinnati, Ohio.

Russell, A. J., Bettendorf Oxygen Hydrogen Co., Bettendorf, Iowa.

Sanderson, J., Laboratory, E. Lloyd, Ltd., Sittingbourne, Kent, England.

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Scheuermann, Theo., 29 Palisade Ave., Garfield, N. J.
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Schimel, Edgar M., 113 So. Division St., Ann Arbor, Mich.

Schneider, Wm. G., 25 Broadway, New York City.

Seaman, William, 2305 18th St., N. W., Washington, D. C.

Sears, Frederick E., 133 College St., Burlington, Vt.

Seffens, Chas. D., 2417 Bancroft Way, Berkeley, Cal.

Sheppard, O. E., 826 Third Ave., South Bozeman, Montana.

Shereshefsky, Juda Laon, 3158 Avalon St., Pittsburgh, Pa.

Shipman, Frank M., 3001 Aubert Ave., Louisville, Ky.

Shrewsbury, Herbert S., Government Lab , Frederick St., Port of Spain, Trinidad, B. W. I.

Shumaker, John B., 4726 N. Hermitage Ave., Chicago, Ill.

Siegel, Alfred, 235 Darragh St., Pittsburgh, Pa.

Skau, Evald L., 56 Lake Place, New Haven, Conn.

Smith, J. Paul, 303 North Park Ave., Buffalo, N. Y.

Smith, Richard M., P. O. Box 367, Gainesville, Florida.

Sneddon, Richard, Dominion Flour Mills Co., 300 St. Ambroise St., Montreal, Quebec, Canada.

Snyder, Clermont J., 128 McAllister St., State College, Pa.

Soff, Le Roy D., 2554 Creston Ave., Bronx, New York City.

Squire, Lyle E., 520 E. Jefferson St., Ann Arbor, Mich.

Stickney, Edward G., 111 Bartlett St., Lewiston, Maine.

Stillman, Albert L., 25 Broad St., General Briquetting Co., New York City.

St. John, Newton D., Gainesville, Florida.

Storr, B. V., 26, The Square, Ilford, London, England.

Stose, Charles W., 1010 Mass. Ave., Apt. 19, Cambridge, Mass.

Street, T. M., Food & Drug Department, Vermillion, S. Dak.

Sullivan, Vernon R., 1514 Chestnut St., Oakland, Cal.

Swallow, Albert Victor, St. Helens Cable & Rubber Co., Ltd., Warrington, England.

Swanson, Walter H., 1726 Van Hise Ave., Madison, Wis.

Swart, Gilbert, 8701 Wallingford Ave., Seattle, Wash.

Swart, Richard H., 22851/2 Gorden Ave., St. Paul, Minn.

Texter, C. R., Mellon Institute, O'Hara St., Pittsburgh, Pa.

Thomas, Raymond E., E. I. du Pond de Nemours Co., Parlin, N. J.

Thomas, Roy Z., Aiken Ave., Rock Hill, S. Car.

Thorpe, Jocelyn Field, Imperial College of Science, South Kensington, London, S. W 7, England.

Towne, Charles C., 102 Orchard St., Newark, N. J.

Treschow, Kenneth F., William Penn Hotel, Pittsburgh, Pa.

Tweedy, Wilbur Rudolph, 120 West Jewell, Salina, Kans.

Tyce, Ludwig A., Duralite Co. Plant, Chula Vista, Cal. Tyler, Walter S., Jr., 430 Pawnee St., Bethlehem, Pa.

Underwood, Wm. Frederick, 106 13th Ave., Columbus, Ohio.

Vardy, Wm. Andrew Shakespeare, Fox Holes Bungalow, Methley, near Leeds, England.

Vivian, Hugh, Messrs Vivian & Sons, Ltd., Swansea, Glam, England.

Vogt, Richard R., 721 Cottage Grove Ave., South Bend, Indiana,

Walker, Lester H., Elm St., Potsdam, N. Y.

Waterman, Ivan R., 2312 College Ave., Berkeley, Cal.

Welch, Isabelle M., 9 W. Melrose St., Chevy Chase, Md.

Wenger, R. G., 48 Ninth East St., Salt Lake City, Utah.

Wilharm, William C., 129 Gordon St., Edgewood, Pittsburgh, Pa.

Williams, George A., Atlantic Christian College, Wilson, N. Car.

Winslow, Arthur F., 307 H. H. Hall, University of Maine, Orono, Maine.

Wood, Henrietta Cooper, 16 Mountwell Ave., Haddonfield, N. J. Wood, James, Cooperative Wholesale Society, Research Dept., 109 Corporation St., Manchester, England.

Woolley, S. W., 42 Cannon St., London, England.

# MEETINGS OF THE SECTIONS

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

### AMES SECTION

On January 11, Victor Lenher, of the University of Wisconsin, spoke on "Selenium and Its Compounds."

On January 17, L. J. Matos, of the National Aniline & Chemical Company, addressed the meeting, his subject being "Dyes and Dyeing."

On January 27, Gerald N. Wendt, research chemist of the Standard Oil Company of Indiana, gave a lecture before the meeting of the Section. His subject was "Rewards of Scientific Research."

At the meeting of the Section, held on January 31, H. E. Howe spoke on "Fundamental Research as a National Factor."

H. M. McLaughlin, Secretary

# CALIFORNIA SECTION

The members of the Section gave a dinner, on February 2, at the Hotel Bellevue, San Francisco, Cal., in honor of E. C. Franklin, of Stanford University, the newly elected president of the American Chemical Society.

L. H. Duschar, Secretary

### CINCINNATI SECTION

The 256th regular meeting of the Section occurred on February 14, when A. P. Mathews, professor of physiological chemistry at the University of Cincinnati, addressed the members on "The Origin of the Organic Substances on the Earth's Surface."

A. O. SNODDY, Secretary

### CLEVELAND SECTION

The regular monthly meeting of the Section, held on January 26, was addressed by C. J. Ramsburg, of the Koppers Company, Pittsburgh, Pa., his subject being "Coke."

On February 21, William J. Hale, of the Dow Chemical Co., Midland, Mich., addressed the Section on the subject of "Our Chemical Awakening."

H. S. BOOTH, Secretary

### COLORADO SECTION

On January 24, W. W. Scott, of the Golden School of Mines, addressed the Section his subject being "Researches in the Catalytic Oxidation of Ammonia."

RUTH B. VERTREES, Secretary

### CONNECTICUT VALLEY SECTION

At the regular monthly meeting of the Section, held on February 10, Amos Bissell, of the Bissell Varnish Company, Bridgeport, Conn., gave an address on "Uses of Varnishes and Baking Japans."

PAUL SEREX, JR., Secretary

### DELAWARE SECTION

On February 21, Brig. Gen. Amos A. Fries, chief of the Chemical Warfare Service, War Department, Washington, D. C., addressed the meeting of the Section, his subject being "Chemical Warfare Materials—What They Are, How Produced, and Peacetime Uses."

J. W. STILMAN, Secretary

# DETROIT SECTION

A joint meeting of the Associated Technical Societies of Detroit, of which the Local Section of the American Chemical Society is a member, was held on January 19. The speaker was Harvey Wiley Corbett, who lectured on "Some Phases of Architectural Development as Affected by Zoning Laws."

The following program was presented before the meeting of the Section on February 21: "General Curricula and Policy of the Cass Technical High School," by E. G. Allen, assistant principal; "The Curricula of the Science Group," by J. C. Moore, head of science group; "The Relation of the School to Industry," by S. R. Wilson, vocational counselor; and an inspection of the Cass Technical High School.

S. R. WILSON, Secretary

### GEORGIA SECTION

On February 15, H. E. Howe, editor of Industrial and Engineering Chemistry, addressed the Section, his subject being "The Policy and Plans of the Society Publications."

L. B. LOCKHART, Secretary

### HAWAHAN SECTION

At a meeting of the Section, held on February 1, D. D. Van Slyke, of the Rockefeller Institute, spoke before the members, taking as his subject "Important Research Investigations Undertaken by the Rockefeller Institute." RONALD Q. SMITH, Secretary

# INDIANA SECTION

On January 9, H. E. Barnard, of the American Institute of Baking, addressed the Section on "The Opportunities for Chemical Research in the Baking Industry." H. E. Howe, editor of Industrial and Engineering Chemistry, was the speaker at the January 23 meeting, when he discussed the various phases of the publications of the Society. I. I. Birdsall, of the General Chemical Company, spoke to the Section at its January 30 meeting on the subject of "Edible Fungi."

At the regular monthly meeting of the Section held on February 9, Albert P. Mathews, of the University of Cincinnati, spoke before the members, his subject being "New Light on the Origin of the Organic Substances on the Earth's Surface."

WILLIAM HIGBURG, Secretary

### IOWA SECTION

The members of the Section were addressed by H. E. Howe, editor of Industrial and Engineering Chemistry, on February 1, his subject being "Publication Problems and Society Procedure."

G. H. COLEMAN, Secretary

### LEXINGTON SECTION

The following officers of the Section have been elected for 1923: J. A. Gunton, president; L. A. Brown, vice president; J. R. Mitchell, second vice president; H. P. Newton, councilor, and E. L. Jackson, secretary-treasurer.

The 85th meeting of the Section was held on February 20, when A. P. Mathews, of the University of Cincinnati, spoke on "The Origin of Organic Substances on the Earth's Surface."

B. I. Jackson, Secretary

# LOUISIANA SECTION

On January 19, H. Z. E. Perkins, of the American Sugar Refining Co., presented a paper entitled "Hydrogen Ion Determination as a Method of Refinery Control." At this meeting the following officers for 1923 were elected: Cassius L. Clay, chairman; S. A. Mahood, vice chairman; C. E. Coates, councilor; H. R. Stevens, secretary-treasurer.

H. R. STEVENS, Secretary

# MAINE SECTION

At the regular meeting of the Section, held on February 12, W. H. Jordan spoke on "Chemistry in the Experiment Stations."

N. E. WOLDMAN, Secretary

# MARYLAND SECTION

The 62nd regular meeting of the Section occurred on January 26. T. B. Hine, of Edgewood Arsenal, presented a paper on "A Few Scientific By-Products of Recent Chemical Warfare Research."

The 63rd meeting of the Section was held on February 23. A lecture, entitled "The Physical and Chemical Properties of Atomic Hydrogen," was delivered by R. W. Wood, of Johns Hopkins University.

About Harvitt, Secretary

### MILWAUKEE SECTION

On February 16, Gerald L. Wendt, of the Standard Oil Company, spoke before the members of the Section, his subject being "Beyond the Microscope."

ALFRED A. CHAMBERS, Secretary

### MINNESOTA SECTION

The 106th regular meeting of the Section was held on January 16, when Edward Bartow, of the University of Iowa, gave an address on "The Activated Sludge Process of Sewage Disposal and its Present Status." The address was illustrated with lantern slides.

The Local Section met with the Northwest Chapter of the American Society for Steel Treating in a joint session, on February 19. The address of the evening was by Paul D. Merica, director of research of the International Nickel Company, his subject being "Nickel, Its Metallurgy and Industrial Applications."

L. M. HENDERSON, Secretary

# NASHVILLE SECTION

The 83rd regular meeting of the Section occurred on January 19, when William Litterer, state bacteriologist and professor of bacteriology, medical department, Vanderbilt University, spoke on "Some Virulent Diphtheria Bacilli in Fowls."

On February 8, H. E. Howe, editor of Industrial and Engineering Chemistry, spoke before the members of the Section, his subject being "Publication Problems and Society Procedure."

H. A. Webb, Secretary

#### NEW HAVEN SECTION

At the regular meeting of the Section, held on February 13, Ellwood Hendrick spoke on "Obligations in Chemistry." The following officers for 1923 were elected: T. B. Johnson, chairman; John F. Hutchinson, vice chairman; H. W. Foote, councilor; John L. Christie, treasurer, and Blair Saxton, secretary.

BLAIR SAXTON, Secretary

# NEW YORK SECTION

A joint meeting of the four chemical organizations in New York City was held on February 9, with the following program: "The Present Situation in the Radium Industry," by Harold E. Bishop, of the Radium Company of Colorado; and "Observations of Industrial Conditions in Europe," by W. S. Landis, of the American Cyanamid Company.

Benjamin T. Brooks, Secretary

# NORTHEASTERN SECTION

The 182nd regular meeting of the Section occurred on February 9, when Charles H. Herty, president of the Synthetic Organic Chemical Manufacturers Association, spoke on "The Present Status of the American Synthetic Organic Chemical Industry."

E. B. MILLARD, Secretary

# NORTHERN INDIANA SECTION

On January 17, F. C. Mathers, of Indiana University, spoke to the Section, his subject being "The Electroplating and Refining of Metals." The following officers for 1923 have been elected by the Section: E. N. Weber, chairman; P. J. Byrne, Jr., vice chairman; J. A. Nieuwland, councilor; M. W. Lyon, Jr., treasurer; and V. C. Bidlack, secretary.

V. C. Bidlack, Secretary

# NORTH CAROLINA SECTION

At a meeting of the Section held on February 14, H. E. Howe, editor of Industrial and Engineering Chemistry, spoke on "The Trend of Scientific Research and its Bearing on Future Civilization." In the afternoon of the same day, Mr. Howe addressed a special meeting of the Section on "Policy, Procedure, Finance and Plans of the Society."

L. B. RHODES, Secretary

### OMAHA SECTION

On December 19, Charles D. Crowley gave an illustrated lecture on "Septic Tanks and Sewage Disposal." The following officers for 1923 were elected by the Section: Charles F. Crowley, chairman; Victor E. Levine, vice chairman; H. A. Senter, councilor; Robert Savage, J. A. Lund and W. D. Yodi, executive committee; and R. N. Perkins, secretary-treasurer.

R. N. Perkins, Secretary

# OREGON SECTION

At the January 27th meeting of the Section, held in Portland, Oreg., F. A. Gilfillan, of the Oregon Agricultural College, spoke on "Chemistry of Synthetic Drugs."

The regular monthly meeting of the Section occurred on February 24, at Corvallis, Oreg. The following papers were read: "Molecular Rearrangement," by E. C. Gilbert; and "The Effect of Temperature and Pressure on Hydrocarbon Vapor," by Floyd E. Rowland.

PAGE R. BOYLES, Secretary

### PHILADELPHIA SECTION

At the regular meeting of the Section, held on February 15, the section was addressed by Robert D. Bonney, of the Congoleum Company, Marcus Hook, Pa.

J. HOWARD GRAHAM, Secretary

# PITTSBURGH SECTION

The Local Section met in joint session with the American Ceramic Society on January 18, the following program being presented: "The Manufacture of Electrical Porcelain," by Marsden H. Hunt, of the Westinghouse High Voltage Insulator Co., Derry, Pa.; "Manufacture and Use of Enamel-Lined Apparatus," by Emerson P. Poste, of the Elyria Enameled Products Co., Elyria, O.; and "Manufacture and Properties of Oven Glass Cooking Ware," by Ralph F. Brenner, of the H. C. Fry Glass Co., Rochester, Pa.

# PUGET SOUND SECTION

On January 23, the Local Section held a joint meeting with the Industrial Bureau of Chamber of Commerce, Seattle, Wash., with the following program: "Recent Improvements in Wood Distillation," by O. F. Stafford, of the University of Oregon; and "A New Explosive from Sawdust," by William Dehn, of the University of Washington.

R. W. Ellison, Secretary

# PURDUE SECTION

At the regular meeting of the Section, held on January 18, B. B. Turner, of Indiana University School of Medicine, gave a lecture on "Life as a Chemical Phenomenon." On February 15, G. N. Hoffer, of the Purdue Experiment Station, spoke on

"Iron and Aluminum in the Corn Plant."

MARGUERITE G. MALLON, Secretary

### RHODE ISLAND SECTION

At the first meeting of the year, held on January 26, George Shannon Forbes, of Harvard University, spoke to the members of the Section, his subject being "Clock Reactions."

On February 20, T. B. Hine, of Edgewood Arsenal, Edgewood, Md., addressed the Section on the subject "Scientific By-Products of Chemical Warfare Research."

NELSON BARLOW, Secretary

### ROCHESTER SECTION

The 148th meeting of the Section occurred on January 22, when Victor C. Chambers, of the University of Rochester, addressed the members on the subject, "The Coloring Matter of Flowers."

On February 2, the members of the Section were invited to attend a lecture by E. V. McCollom, given before the Tuberculosis and Public Health Association of Rochester, N. Y., his subject being "Diet and Health."

The 149th regular meeting was held on February 5, when L. Ray Fergusen, of the Genesee Pure Food Co., LeRoy, N. Y., spoke on "Chemistry in the Jelly-Powder Industry."

At a joint meeting of the local Section with the Rochester Academy of Science, and Rochester Section of the Optical Society of America, held on February 19, Fred E. Wright, of the Geophysical Laboratory, Washington, D. C., spoke on "The Role of Experiment in Geology."

EARLE M. BILLINGS, Secretary

#### SAINT LOUIS SECTION

On February 7, H. E. Howe, editor of Industrial and Engineering Chemistry, spoke before the meeting of the Section, his subject being "Policy, Procedure, Finance and Plans of the Society."

H. A. Carlton, Secretary

# SAVANNAH SECTION

The regular monthly meeting of the Section occurred on January 11, when J. W. Daniels, of Savannah, spoke before the members on the subject, "Acidosis and Alkalosis."

HERBERT P. STRACK, Secretary

### SOUTHEAST TEXAS SECTION

On February 22, G. L. Fulgate, assistant city engineer of the City of Houston, Texas, addressed the Section, his subject being "Activated Sludge Process of Sewage Disposal." At this meeting, H. E. Howe, editor of *Industrial and Engineering Chemistry*, spoke on "Policy, Procedure, Finances and Plans of the Journal."

P. S. TILSON, Secretary

### SOUTHERN CALIFORNIA SECTION

The address before the Section, January 25, was by J. Jakobsen, on "The Refining and Hydrogenation of Edible Vegetable Oils." On February 15, F. B. Ortman spoke to the members, his subject being "Recent Developments in the Field of Ceramics."

MARK WALKER, Secretary

# SYRACUSE SECTION

On Saturday afternoon, January 13, the local Section enjoyed a pleasant trip through the gas plant of the Syracuse Lighting Co.

W. B. Hicks, Secretary

### TOLEDO SECTION

The 51st meeting of the Section occurred on January 20, when H. E. Howe, editor of Industrial and Engineering Chemistry, spoke on "Problems in Scientific Publication."

GUY E. VAN SICKLE, Secretary

# UNIVERSITY OF ILLINOIS SECTION

At the meeting of the Section, held on February 20, C. W. Balke, of the Fansteel Products Co., North Chicago, Illinois, addressed the members on the subject, "Ductile Tantalum."

D. T. Englis, Secretary

# VIRGINIA SECTION

At the 54th regular meeting of the Section, held on January 12, E. C. L. Miller, of the Medical College of Virginia, addressed the members, his subject being "Bacterio-phage."

On February 9, Graham Edgar, of the University of Virginia, spoke before the members of the Section, his subject being "Atomic Weights, Isotopes, and the Breaking up of Atoms."

W. G. Crockett, Secretary

## WASHINGTON, D. C. SECTION

The 337th meeting of the Section occurred on January 11, when R. C. Wells spoke on "Chemistry of the Sea."

The 339th meeting of the Section was held on February 8. E. V. McCollum spoke on "What has been Learned about Nutrition in a Decade."

J. B. Reed, Secretary

#### WESTERN NEW YORK SECTION

On January 10, the Section held a New Year's meeting at Canisius College.

On February 7, Rev. George L. Coyle, head of the Department of Chemistry, Holy Cross College, Worcester, Mass., addressed the members of the Section taking as his subject, "Activities of the American Chemical Society Committee on Society Procedure."

At the meeting held on February 15, T. A. Boyd spoke on "The Application of Chemistry to the Elimination of Fuel Knock."

R. W. Hess, Secretary

## WISCONSIN SECTION

At the regular meeting of the Section, held on January 10, W. Lee Lewis, of Northwestern University, spoke on "The Organic Chemist at Work."

The following officers for 1923 have been elected: J. H. Mathews, chairman; A. J. Marschall, vice chairman; F. Daniels, secretary-treasurer; L. F. Hawley and Victor Lenher, councilors.

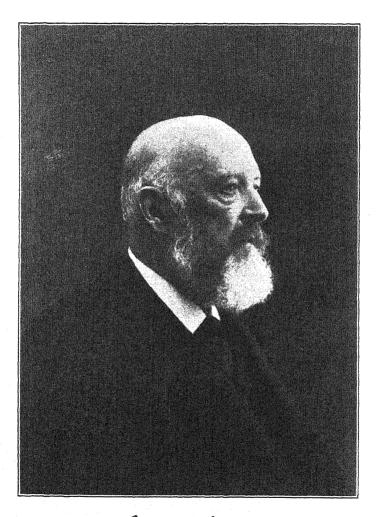
The regular meeting of the Section was held on February 14, when Joel Stebbins, professor of Astronomy at the Washburn Observatory, spoke to the members. His subject was "The Chemistry of the Stars."

FARRINGTON DANIELS, Secretary

## DECEASED

Arnold, Frank L., 32 School St., Woburn, Mass. Died, 1922.
Browning, Jr., Charles, c/o Southern Pacific Lines, Sacramento, Cal. Died, January 13, 1923.
Emerson, Herbert C., 145 Chestnut St., Springfield, Mass. Died, December, 1922.
Evans, Robert W., Mead Pulp & Paper Co., Chillicothe, O. Died, 1922.
Haines, Walter S., Rush Medical College, Chicago, Ill. Died, January 27, 1923.
Heilbrum, Alexander L., 1229 Webster Bldg., Chicago, Ill. Died July 11, 1922.
Huntington, Harwood, 419 S. Lorraine Blvd., Los Angeles, Cal. Died, 1923.
Lunge, George, 37 Carmenstrasse, Zurich, Switzerland. Died, January 3, 1923.
Mason, Francis Payne, 806 Marquette Bldg., Chicago, Ill. Died, Nov. 10, 1922.
Newberry, Spencer Baird, 818 Engineers Bldg., Cleveland, O. Died, Novelo, 1922.
Patterson, C. A., 1007 Broome St., Wilmington, Del. Died, July 26, 1922.
Tucker, Willis Gaylord, 80 Howard St., Albany, N. V. Died, April 22, 1922.





Höoff Baeyer

# ADOLF VON BAEYER

# 1835-1917

With the death on August 20, 1917, of Adolf von Baeyer, there passed the last of the great founders of organic chemistry. Less than two years before, on his eightieth birthday, he retired from his professorship, having up to that time carried on his full work in lectures and laboratory supervision. So active was he that it is doubtful if he would even then have given up his labors, had not the war depleted his laboratory of students and robbed him of his laboratory staff.

It was just before this time that his many American admirers were not a little shocked to find his name heading the list of German savants in the celebrated manifesto, calling on their colleagues outside of Germany to withhold judgment regarding the Belgian atrocities. He was known to have long been opposed to the militaristic spirit of Prussia, and it had been assumed that his refusal to accept the call to Berlin, the home of his childhood, as successor of Hofmann, was inspired by this disapproval. But in his old age, it is hardly surprising to find him testifying to his loyalty to that *Vaterland*, under which he had lived for well-nigh four score years. It was an alphabetical mischance that gave the manifesto publicity as that of "Adolf von Baeyer and others." We may believe that he was well content to retire to his beautiful home on the Starnbergersee, and pass the few remaining months of his life in well-earned quiet and comfort.

Comparatively few Americans studied with Baeyer. At the time when his brilliant work on indigo would naturally have begun to attract students to Munich, Victor Meyer was at Göttingen and Ostwald was beginning his great activity at Leipzig, Hofmann and numerous others were at Berlin, and the stream of American students was never largely diverted to the south; few of us knew anything of the personality of the man. One, however, whose good fortune it was to spend a year in his laboratory has written me the following:

"He impressed me at the time I was in his laboratory, and I retained that impression afterwards, as being a man of a great deal of personal dignity. He was handsome, with a large head and very expressive eyes. As regards the students in the laboratory he was rather distant, but very gracious and approachable to the English and Americans. His lectures, which were brilliantly illustrated by experiments, were models of simplicity; he always emphasized the important general reactions and properties of substances, and appealed in general to those who had but little previous knowledge of the subject. In this respect he was the very opposite of Victor Meyer, who lectured as if the class consisted entirely of students familiar with organic chemistry from previous training. Professor Baeyer was good enough to write me from time to time, and I saw him again in 1913, when he was ready to retire from active duties. In spite of his advanced age, he was remarkably familiar with all the modern literature. There was a strain of mysticism in his talk, which indicated somewhat that he was losing his sense of logic."

Adolf von Baeyer was born at Berlin, October 31, 1835, his father being at the time chief of the Geodetic Institute, and we are not surprised to find that even as a child he was interested in natural science. His private laboratory at home seems not always to have been appreciated, for Paul Heyse, who was an intimate in the family, wrote:

"Es stinkt in diesem Huss gar sehr, Das kommt vom Adolf Baeyer her."

He began his serious chemical studies under Bunsen at Heidelberg, and later was under Kekulé, whom he followed to Ghent. He took his degree of Ph.D. at Berlin in 1858, and there came under the influence of Hofmann, with whom he worked as Privat-dozent, and in 1866 he became "extraordinary" professor. It was during this period that he carried on his studies on organic arsenic compounds, inspired by Bunsen, and on which he made his doctor's thesis. At this time also he did fundamental work on the constitution of uric acid, actually synthesizing "pseudo-uric acid" (the ureid of alloxan). While his view of the structure of uric acid was somewhat at fault, he rightly believed that if he could remove a molecule of water from pseudo-uric acid he would have uric acid. In spite of great efforts he failed to accomplish this dehydration, and only in 1888 did Emil Fischer, trained in Baever's own laboratory, succeed, by dissolving pseudouric acid in fused oxalic acid, in carrying out this operation and completing the synthesis along Baeyer's lines. During this period, also, he began his work on the structure and synthesis of indigo, which was brought to completion a quarter of a century later.

In 1872, Baeyer was called from Berlin to head the department of chemistry in the new University of Strasburg. In the 3 years he remained here his work upon the phthaleins was perhaps the most important, but more far-reaching was the impetus he gave to Emil Fischer, the greatest of his students. Caro also began his work with him during this period.

Strasburg was, however, soon to be deprived of his services, for in 1875 he was chosen Liebig's successor at Munich, where he founded the *Chemisches Institut*. Here his greatest work was done, work great in the importance and extent of his researches and even greater in the stream of students he sent forth, a stream of those who have largely made organic chemistry what it is to-day.

It would require a book to give a review of Baeyer's contributions to organic chemistry. His *Gesammelte Werke*, published in Braunschweig in honor of his seventieth birthday, occupy two volumes, and these works are classified under no less than 17 different heads. There was hardly a field in the organic chemistry of the last century that he did not cultivate and leave the richer for his work. Of far-reaching importance were his contributions to the structure of benzene. He was probably the first to propose a symmetrical structure for the molecule, basing his argument

on the formation of mesitylene from acetone; his work on oxyterephthalic acid and the hydrophthalic acids settled the case against Ladenburg's prismatic formula, as well as against the diagonal formula of Claus. His own "centric" formula, perhaps first suggested by Armstrong, and widely adopted as a tentative solution of the problem, was a keen and successful effort to "beg the question" in a scientific way. He saw clearly that no one formula would account for all the reactions. The idea that the same molecule could exist with different constitutions at different times or under different circumstances, had been earlier introduced by Baeyer under the name of pseudomerism, to account for the then puzzling anomalous reactions of aceto-acetic ester, and was later developed under the name of tautomerism, now a well-recognized phenomenon of chemistry. It was his work in connection with the structure of benzene that led him later to formulate his strain theory (Spannungstheorie) of the double and triple bond, especially between carbon atoms, a theory which has exercised an important influence on the development of chemistry.

Baeyer was always closely identified with the Deutsche Chemische Gesellschaft, and gave the opening paper at its first meeting, January 27, 1868. his subject being the reduction of indigo to indole by means of zinc dust. This was the first of many papers before the society, in which he portrayed, for the next score of years, his efforts to solve the problem of first the constitution and then the synthesis of indigo. It is this work by which Baever is best known to the world outside. It is interesting to recall that even after Baeyer had completed this work, it was still a mooted question whether synthetic indigo was really the same as that produced by the plant. similar controversy had raged regarding natural and synthetic alizarin, the first step in elucidating the constitution of which had been made possible to Graebe and Liebermann, by the use of the zinc dust reaction introduced by Baeyer. The differing color reactions of benzene from benzoic acid and that from coal tar was another case in point, and I recall that it was often discussed in the Göttingen Laboratory in the early 80's. It was there that Victor Meyer's discovery of thiophene in commercial benzene revealed the importance of minute amounts of impurities in the natural substances, and settled the controversy regarding the absolute identity of natural and synthetic products. All of this may justly be considered an outgrowth of Baeyer's work.

Though at no little distance from Berlin, the headquarters of the Gesell-schaft, Baeyer was always in close touch. His many papers in the Berichte constitute alone no mean history of the rise and development of organic chemistry. He was repeatedly honored by the Society by election to its offices, and often greeted officially on the various anniversary days of his life. It was on the occasion of the celebration of his seventieth birthday that van't Hoff, then president of the Gesellschaft, and Liebermann

presented him with an address, in which, after alluding to his work on indigo, his services to organic chemistry were well summarized, as follows:

"But even these great attainments constitute but a limited portion of the work accomplished through your marvelous intuition and incomparable experimental skill. As by analysis you have unlocked the secrets of uric acid, isatin and mellite, so on the other hand you have taught us by synthesis the preparation, now of important compounds such as neurine, and now of whole series of condensation products, among which are found the phthaleins, the beautiful fluorescein and eosin, gallein, cerulein and quinizarin. Cinnamic acid led you on the one hand to indigo, on the other to the synthesis of quinoline and rings containing nitrogen. Linked with this, your sharp-sighted strain theory as well as your theories of pseudomerism and of *cis-trans*-isomerism, have revealed to us new laws that are now well recognized. Proceeding from the latest explanations of the benzene nucleus, you are opening up the nature of the hydro-aromatic compounds and the fundamental structure of the terpenes, whose simpler members you have been happily enabled to synthesize. It is only natural that we should be looking with eager anticipation to the progress of your latest work, which has for its aim nothing less than the clearing up of the connection between color and constitution."

Baeyer had nearly reached his three score years and ten when, with Villiger, he began his far-reaching work on the oxonium bases and the quadrivalent nature of oxygen, and at about the same period came the discovery of triphenylmethyl, the investigation of which has been so largely carried on by Gomberg.

Baeyer's was a life of great achievements, but any notice of him would be incomplete which did not emphasize his extraordinary power of inciting his students to follow in his footsteps. A roll of those who have been students in his laboratory would include almost every professor of chemistry in the German universities from 1880 to 1910. Claisen, Curtius, Emil and Otto Fischer, Graebe, Knorr, Liebermann, Victor Meyer and Willstätter are but a few among many. As leaders in industrial chemistry, too, his students have played no insignificant part, as witness the work of Caro and of Duisberg.

Adolf von Baeyer was a great chemist; great as a student, great as an investigator, great as a teacher; the American Chemical Society honored itself when his name was placed upon its roll of Honorary Members.

JAMES LEWIS HOWE

# Proceedings

## COUNCIL

The committee to suggest rules governing the selection of the chemist who is annually deemed most worthy to receive the prize given by the Allied Chemical and Dye Corporation, as published on page 88 of the Proceedings for 1922, consists of Edgar F. Smith, chairman, Charles F. Chandler, Edward W. Morley, Ira Remsen, and F. P. Venable. They will report at the New Haven meeting.

# REPORT OF THE TREASURER

The Treasurer begs your indulgence for the delay in making his report, due to his absence.

The Auditors' Report was published in the March Journal. There has been no change in the permanent securities held by the Society excepting the expiration of \$10,000 Victory Loan Bonds on December 15. Since the beginning of this year this amount has been replaced in the fund by the purchase of Liberty Bonds.

An examination of the Auditors' Report shows total receipts from the usual sources of about \$308,000 and total disbursements of about \$298,000, leaving a net excess of receipts over disbursements of \$9,730.44. It should be noted, however, that in the Auditors' Report the receipts from Advertising are included for 13 months. It has been customary heretofore to report December receipts, for example, as of January first date. For this year, however, the December 1921 receipts are reported as of January first date, and by a change in method December 1922 receipts are reported as of December 30 date and so included in the records for the year 1922. If we deduct the receipts for one December we find that our working profit would have been slightly less than \$2,000.

It may be of interest to some members to give a percentage analysis of our receipts and dispursements.

RECEIPTS of \$308,000 were divided as follows, in round numbers:

Members' Dues	57 %
Advertising, net	29 %
Non-Member Subscriptions	7 %
Interest	2.3%
Back Numbers	2 %
Postage	1.3%
Reprints	1.2%

DISBURSEMENTS of about \$298,000 were distributed as follows, percentages being given as percentages of receipts:

Chemical Abstracts	32%
Industrial Journal	23%
Journal A. C. S	15%
Printing Advertising	10%
Secretary's Office	7%
News Service	3%
Local Sections	3%
Treasurer's Office	1%
Surplus	30%

Other items are less than 1%.

We are rapidly approaching the day when the cost of the Industrial Journal plus the cost of the advertising printed in it will be covered by the receipts from advertising in that journal plus the receipts of non-member subscriptions to the journal. We have not yet quite reached the point, but are near it.

For the year 1923 the Budget as drawn by the Directors shows an excess of proposed disbursements over expected income. As the price of paper shows indications of rising further, great care will be needed this year to come through the year with a balanced budget.

JOHN E. TEEPLE
Treasurer

March 12, 1923

Dr. John E. Teeple, Treasurer
American Chemical Society
50 East 41st Street,
New York City

## DEAR SIR:

As requested by you we have this day made an inspection and count of the securities held by the American Chemical Society as investments; also those held as trust funds, as such securities are enumerated in Exhibit "A" of our report, dated January 18th, 1923.

A certified list of these securites was furnished us by you at the time of rendering our report, which list has now been verified by an inspection and count of the securities. All of the securities were found to be on hand, or properly accounted for.

Yours very truly, McCulloh & Brown

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Wilkie, John B., 2205 Capitol Ave., Des Moines, Iowa.

Williams, C. W., Ky Oxygen Hydrogen Co., Logan & Goss St., Louisville, Ky.

Williams, Howell, Osram G. E. C. Lamp Works, Hammersmith, London W. 6, England.

Wilson, Joshua T., Box 273, Grove City, Pa.

Wolfson, Jacob. National Aniline & Chem. Co., 351 Abbott Road, Buffalo, N. Y.

Wood, Harry A., Santa Elena, Entre Rio, Argentine Republic.

Work, Harold K., 835 Livingston Hall, Columbia Univ., New York City.

Working, Earl B., Desert Laboratory, Drawer L., Tucson, Ariz.

Wright, E. Katharine, North Caroline College for Women, Greensboro, North Carol.

Wylde, Edward P., 6330 Kimbark Ave., Chicago, Ill.

Yant, William P., 4740 Friendship Ave., Pittsburgh, Pa.

Yen, Louis, 110 Cook St., Ithaca, N. Y.

#### CORPORATION MEMBERS ELECTED

British American Oil Co., Ltd., Royal Bank Building, Toronto, Canada. Corning Glass Works, Corning, N. Y. Hudson Coal Company, 206 East Market St., Scranton, Pa. Industrial Fibre Company, West 98th and Walford Ave., Cleveland, Ohio.

# MEETINGS OF THE SECTIONS

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

### AKRON SECTION

The first meeting of the Section was held on February 26, when Harry N. Holmes, of Oberlin College, spoke on "Emulsions."

W. J. Kelly, Secretary

### CALIFORNIA SECTION

The 137th regular meeting of the Section occurred on March 2, at the Engineers' Club, San Francisco, Cal. Two papers, as follows, were delivered: "Equilibria in Solutions Containing Carbonates and Chlorides of Sodium and Potassium," by W. C. Blasdale, of the University of California; and, "Manufacture and Purification of Oil Gas," by George H. West, chemical Engineer, of San Francisco.

L. H. DUSCHAR, Secretary

#### CHICAGO SECTION

At the regular meeting of the Section, on February 23, William Hoskins, of Chicago, addressed the members on the subject, "Experiences of a Consulting Chemist." The usual group meetings were held.

S. L. Redman, Secretary

## COLORADO SECTION

The Feburary meeting of the Section was held on the 28th at the Denver Public Library, Denver, Colo. A paper, entitled "Some Aspects of the Rare Earths," by Earle Engle, of Denver University, was presented.

RUTH B. VERTREES, Secretary

## CONNECTICUT VALLEY SECTION

On March 10, Ellwood Hendrick, consulting editor of Chemical and Metallurgical Engineering, New York City, addressed the members of the Section, his subject being "Obligations in Chemistry."

PAUL SEREX, JR., Secretary

## CORNELL SECTION

At a meeting of the Section, held on March 19, Victor F. Hess, of the United States Radium Corporation, addressed the members, his subject being "Radium Emanation and its Purification."

On March 23, A. C. Boniface, of the Foamite Childs Corporation, delivered an illustrated lecture before the Section, his subject being "The Use of Froth for Fighting Fires."

F. E. Hance, Secretary

## DELAWARE SECTION

The regular monthly meeting of the Section, held on March 21, was addressed by Marston T. Bogert, of Columbia University. His subject was "Perfumes, Natural and Synthetic."

J. W. Stillman, Secretary

#### EASTERN NEW YORK SECTION

On March 9, Walter Rosenhain, director of the metallurgical department of the National Physical Laboratory of England, delivered a lecture before the meeting of the Section. His subject was "The Relation Between the Properties and Structure of Metals."

E. H. Darby, Secretary

#### GEORGIA SECTION

The following officers have been elected by the Section for the year 1923: Chairman, J. F. Sellers; vice chairman, J. S. Brogdon; secretary-treasurer, L. B. Lockhart; and councilor, W. P. Heath.

L. B. LOCKHART, Secretary

#### INDIANA SECTION

On February 13, Neil Waterbury, of the Link Belt Co., spoke before the members of the Section, his subject being "Malleable Cast Iron and Its Properties." At the meeting of February 20, Frank B. Wade, of Shortridge High School, talked on "Color in Precious Stones."

The regular monthly meeting of the Section occurred on March 9, at Indianapolis, Ind. L. M. Tolman, technical director, Wilson & Company, Chicago, Ill., spoke on "The Value of Meat in the Diet."

WILLIAM HIOBURG, Secretary

## KANSAS CITY SECTION

At a meeting of the Section, held at Lawrence, Kansas, March 16, Roger Adams, professor of organic chemistry, University of Illinois, spoke on "Synthetic Drugs." On the same day, Prof. Adams addressed a meeting in Kansas City, taking as his subject "Recent Developments and Recent Patents in the Field of Organic Chemistry."

LEE E. CLARK, Secretary

#### LEXINGTON SECTION

The S6th regular meeting of the Section occurred on March 14, when O. M. Shedd, research chemist in the Kentucky Agricultural Experiment Station, Lexington, Ky., spoke on "The Relation of Sulfur to Soil Fertility." E. L. Jackson, Secretary

## LOUISIANA SECTION

On February 21, H. E. Howe, editor of Industrial and Engineering Chemistry, addressed the Section, his subject being "Publication Problems and Society Procedure."

H. R. STEVENS, Secretary

# LOUISVILLE SECTION

The January meeting of the Section was held on the 18th, and was addressed by W. R. Jillson, director of the Kentucky Geological Survey. His subject was "The Geology of Oil and Gas in Kentucky."

C. E. Geiger, Secretary

## MAINE SECTION

At the regular monthly meeting of the Section, held on March 9, E. W. Manter, of the Westinghouse Electric and Manufacturing Co., spoke on "Industrial Lighting (Illustrated)."

N. E. WOLDMAN, Secretary

#### MIDLAND SECTION

The 16th regular meeting of the Section was held on February 21, when E. R. MacLaughlin of the Dow Chemical Co., spoke on "Evaporator Studies."

John A. Gann, Secretary

#### MINNESOTA SECTION

On January 30, H. E. Howe spoke before the meeting of the Section, his subject being "Publication Problems and Society Procedure."

L. M. Henderson, Secretary

# NEBRASKA SECTION

The 107th meeting of the Section occurred on February 3, when H. E. Howe, editor of Industrial and Engineering Chemistry, spoke on "Publication Problems and Society Procedure."

S. B. Arenson, Secretary

## NEW YORK SECTION

The regular meeting of the Section was held on March 9. The Nichols Medal was presented to Thomas Midgley, of the General Motors Research Corporation. The program was as follows: "Introductory Remarks," by C. A. Browne, chairman of the Section; "Midgley and his Work," by W. D. Bancroft, of Cornell University; "Presentation of the Nichols Medal," by Charles H. Herty, president of the Association of Synthetic Organic Chemical Manufacturers; and acceptance and address by Thomas Midgley, "Some Fundamental Relations Among the Elements and Compounds as Regards the Suppression of Gaseous Detonation."

Benjamin T. Brooks, Secretary

## NORTHEASTERN SECTION

The 183rd meeting of the Section occurred on March 9, when Otto Folin, of the Harvard Medical School, spoke on "The Metabolism of Uric Acid."

E. B. MILLARD, Secretary

#### NORTHERN INDIANA SECTION

On February 21, R. E. Wilson, director of research, Standard Oil Co., Whiting, Ind., spoke to the Section, his subject being "The Mechanism of the Corrosion of Iron and Steel."

V. C. Bidlack, Secretary

#### OMAHA SECTION

The members of the Section were invited to be the guests of The Cudahy Packing Company to attend a dinner, scientific program, exhibit, and laboratory tour on March 6. At the scientific meeting the following program was presented: "Historical Aspects of the Meat Packing Industry," by C. A. Stewart; "The Role of Bacteriology in the Meat Packing Industry," by Millard Langfeld; "The Role of Chemistry in the Meat Packing Industry," by P. G. Daschavsky; "The Bacteriology of Meat Curing Solutions," by W. S. Sturgis; and "The Chemistry of Meat Curing Solutions," by H. L. Cox.

R. N. PERKINS, Secretary

# PHILADELPHIA SECTION

At the regular monthly meeting of the Section, held on February 15, the following papers were presented: "The Artificial Silk Industry," by Hugo Schlatter; and "A Rapid Testing Method for Paint and Similar Plastics," by Robert D. Bonney.

On March 15, Oswald Schreiner, of the Department of Agriculture, addressed the meeting of the Section, his subject being "Chemistry and Agriculture." At the same meeting, Charles C. Roberts spoke on "A Clever Method for Elimination of Moisture."

J. HOWARD GRAHAM, Secretary

#### PITTSBURGH SECTION

The annual smoker of the Section was held on February 22 at the U. S. Bureau of Mines auditorium, Pittsburgh, Pa. An interesting program of entertainment was provided.

E. S. STATELER, Secretary

#### PUGET SOUND SECTION

At the regular monthly meeting of the Section, G. C. Howard, of Seattle, Wash., spoke on "Tannin, Cork and other Products from Bark." R. W. Ellison, Secretary

#### RHODE ISLAND SECTION

On March 6, Ralph H. McKee, of Columbia University, lectured before the members of the Section. His subject was "Future Sources of Gasoline: Will the Supply Hold Out?"

Nelson Barlow, Secretary

#### ROCHESTER SECTION

The 152nd regular meeting of the Section, held on March 19, was addressed by Breese Jones, his subject being "Protein Factor in Nutrition (Illustrated)."

ERLE M. BILLINGS, Secretary

# SAINT LOUIS SECTION

The following program was presented at the meeting of the Section held, on March 5: "The Standardization of Chemical Apparatus," by B. F. Glasser, of the Henry Heil Chemical Company; and "Some Observations on the Situation in Europe," by Gaston Du Bois, of the Monsanto Chemical Works.

On March 24, E. C. Franklin, president of the American Chemical Society, gave a lecture before the members, his subject being "The Ammonia System of Compounds."

H. A. CARLTON, Secretary

# SAVANNAH SECTION

At the regular meeting of the Section, held on Feburary 14, V. H. Bassett spoke on "The Life and Work of Pasteur." This was followed by a talk on "Industrial and Engineering Chemistry," by H. E. Howe, editor.

Herbert P. Strack, Secretary

#### SOUTHERN CALIFORNIA SECTION

The March meeting of the Section was held on the 16th, when E. C. Franklin, president of the American Chemical Society, spoke on "The Ammonia System of Compounds."

MARK WALKER, Secretary

## SOUTH JERSEY SECTION

The regular meeting of the Section was held on March 15, when John H. Muller, of the University of Pennsylvania, spoke on the subject, "Germanium."

W. FLETCHER TWOMBLY, Secretary

# SYRACUSE SECTION

On February 23, John A. Palmer, of Auburn, N. Y., addressed the members of the Section. His subject was "Linoleum and Drying Oils."

At the regular meeting held on March 9, Harry Essex, professor of Physical chemistry, Syracuse University, spoke to the members on the subject of "Isotopes."

W. B. HICKS, Secretary

#### TOLEDO SECTION

The regular March meeting of the Section, held on March 7, was addressed by T. A. Boyd, of the General Motors Research Corporation. His subject was "The Application of Chemistry to the Elimination of the Fuel Knock."

Guy E. Van Siere, Secretary

#### UNIVERSITY OF MICHIGAN SECTION

On February 27, E. H. Kraus spoke before the members of the Section, his subject being "Some Recent Tendencies in Mineralogy."

At the regular March meeting of the Section, held on the 13th, J. E. Harris, of the Western Electric Company, spoke on "The Electron at Work."

C. C. MELOCHE, Secretary

#### UNIVERSITY OF MISSOURI SECTION

The 114th meeting of the Section, held on February 6, was addressed by H. E. Howe, editor of Industrial and Engineering Chemistry, his subject being "Publication Problems and Society Procedure."

H. E. French, Secretary

## VERMONT SECTION

At the regular monthly meeting of the Section, held on February 16, P. Conant Voter, of Middlebury College, spoke on "The Atomic Weight of Arsenic." At the same meeting, Elbridge C. Jacobs, of the University of Vermont, spoke on "Origin of the Vermont Talc Deposits."

E. C. Jacobs, Secretary

## VIRGINIA SECTION

On March 9, at the Medical College of Virginia, Richmond, Va., W. M. Corse, of the National Research Council, addressed the Section, his subject being "Nickel, Its Metallurgy and Uses."

W. G. Crockett, Secretary

## WASHINGTON, D. C. SECTION

The 339th meeting of the Section occurred on March 8, when Leason H. Adams, of the Geophysical Laboratory, spoke on "Reactions and Properties of Substances at High Pressures."

J. B. Reed, Secretary

## WESTERN NEW YORK SECTION

"Blue Eyes and Blue Feathers," was the subject of a lecture by W. D. Bancroft, of Cornell University, before the local Section, at its meeting held on March 8.

R. W. HESS, Secretary

## WISCONSIN SECTION

The 122nd regular meeting of the Section was held on March 14, when George I. Kemmerer spoke on "A Scientific Study of Fresh Water Lakes."

FARRINGTON DANIELS, Secretary

#### DECEASED

Dunham, Edward K., Seal Harbor, Maine. Died, April, 1922.
Hurley, John, 507 Maine St., Little Falls, N. Y.
Morley, Edward W., West Hartford, Conn. Died, February 24, 1923.
Price, Arthur F., 2 Pine St., San Francisco, Cal.
Smoley, A. R., Nucoa Butter Co., Bayonne, N. J.
Thurston, Azor, Grand Rapids, Ohio. Died, March 4, 1923.
Toon, James R., San Lorenzo, Cal. Died, June, 1922.
Waddell, John, School of Mines, Kingston, Ontario, Canada.
Woegerer, Carl V., 20 West 25th St., New York, N. Y.

# Proceedings

# GENERAL MEETING MINUTES

The 65th general meeting of the American Chemical Society was held at NewHaven, Connecticut, Monday, April 2 to Saturday, April 7, 1923, inclusive. The Council Meeting was held on the 2nd, the general meeting on the morning and afternoon of the 3rd, and divisional meetings all day Thursday and Friday. Excursions took up the whole of Saturday. These excursions covered numerous manufacturing plants not only in New Haven but in the surrounding cities and towns. A feature of the meeting was the dedication of the Sterling Chemistry Laboratory which was under the auspices of Yale University and to which all day Wednesday was given. A second Council meeting was held on Wednesday afternoon with the approval of the authorities at Yale. Full details of the meeting will be found in the May, 1923, issue of *Industrial and Engineering Chemistry*. The registration was slightly over 1200, with approximately 100 ladies attending the meeting. A considerable number of members, estimated at 200, the meeting who, coming in the last two days, did not register, not realizing the necessity attended of registering and paying the registration fee to help carry the expense of the meeting, as voted by the Council.

A general public address entitled "Chemistry and the Public" was given by Francis P. Garvan on Tuesday morning. Sir J. J. Thomson addressed the Society on Wednesday evening on "The Unity of Physics and Chemistry."

At the general business meeting held Tuesday morning resolutions and tribute were presented to our late Honorary Member, Edward W. Morley. These resolutions will be found printed in the Council Minutes.

At the general meeting on Tuesday afternoon the following general papers were presented:

Carl L. Alsberg. Chemistry and Our Food Resources.

C. O. Johns. The History and Status of Chemistry Petroleum Research.

H. E. Barnard. The Baker Turns to the Chemist.

Oskar Baudisch. The Influence of Light on Inorganic Material and Life Processes.

W. O. Mitscherling. Cellulose Silk.

Arthur Hirschfelder. The Influence of Modern Chemistry on Pharmacology.

The following Divisions and Sections met: Divisions of Agricultural and Food Chemistry, Biological Chemistry, Cellulose Chemistry, Dye Chemistry, Industrial and Engineering Chemistry, Chemistry of Medicinal Products, Organic Chemistry, Petroleum Chemistry, Physical and Inorganic Chemistry, Rubber Chemistry, Sugar Chemistry, Water, Sewage and Sanitation; Sections of Chemical Education, Gas and Fuel Chemistry, and History of Chemistry. Further details of their meetings will be found in the May issue of *Industrial and Engineering Chemistry*.

On Monday evening a complimentary banquet to the Council, attended also by many members of the Society and a large number of the members of the New Haven Chamber of Commerce, was given by the New Haven Chamber of Commerce to the Council at the Taft Hotel. Many speakers of prominence addressed the members. The banquet was an occasion long to be remembered by those who were fortunate enough to attend.

On Tuesday evening a very enjoyable smoker was tendered by the New Haven and Connecticut Valley Sections in the dining hall of Yale University. The special feature was a dramatical allegory entitled "Iono and Faradette, A Chemical Ballet,"

written by Daniel Caldwell Long and John Arrend Timm. The play was beautifully staged, was extremely interesting, and was thoroughly appreciated by all present.

At the dedication exercises at Sterling Chemistry Laboratory the gathering was addressed by Past President Edgar F. Smith on "The History of Chemistry in America with Special Reference to Yale." The building was presented to the University by the Sterling Trustees and accepted by President Angell with proper reply. President Franklin replied also for the Society when it was presented to the Society for its use during the meeting. The University tendered a complimentary luncheon to all members and guests the same day at one o'clock in the University dining hall.

On the evening of the 5th an indoor polo game was staged for the members in the Yale Armory. On the 6th a reception and dinner was given to the members and guests in Woolsey Hall. The scientific program was extensive, 375 papers being presented.

CHARLES L. PARSONS, Secretary

# DIRECTORS' MINUTES

The Directors of the American Chemical Society met in the Hotel Taft, New Haven, Conn., Monday, April 2, 1923, at 10:30 p.m., with E. C. Franklin in the Chair, and W. D. Bancroft, William Hoskins, John E. Teeple, and C. L. Parsons present.

The Treasurer reported the following transactions:

- Dec. 15, 1922 \$10,000 Victory Liberty Loan Bonds, called, paid to-day.
- Dec. 15, 1922 \$25,000 Note dated 11/9/22, Farmers' Loan & Trust Co. paid to-day— Total \$25,118.75.
- Dec. 15, 1922 Bought \$800 Fourth Liberty Loan Bonds, investing Priestley Memorial Funds—Total \$795.65.
- Jan. 5, 1923 Bought \$10,000 Third Liberty Loan Bonds, replacing the \$10,000 Victory called Bonds 12/15/22—Total \$10,041.90.
- Jan. 13, 1923 Bought \$10,000 Victory Liberty Bonds, due May 20, 1923, Temporary Investments—Total \$10,079.40.
- Jan. 26, 1923 Bought \$10,000 Victory Liberty Bonds, due May 20, 1923, Temporary Investments—Total \$10,092.56.
- Mar. 29, 1923 Bought \$600 par Liberty Third Bonds—Life Membership Fund— Total \$591.51.

It was voted that the Treasurer be authorized to expend not to exceed \$600.00 in furnishing a booth at the Chemical Exposition and arranging a proper exhibit therein.

It was voted, in view of the fact that accounts have been fully audited and much useless material accumulates, that the Treasurer be authorized to destroy obsolete records, canceled checks, etc. of his office prior to the year 1921 and to do likewise in future years for similar records of the years prior to two years previous to the year current.

It was voted to rescind the vote of the Directors passed on November 22 regarding special reprints such as theses and that hereafter these special reprints be handled by the printer as heretofore but that the prices charged by the printer be subject to revision by the Society.

CHARLES L. PARSONS, Secretary

## ADVISORY COMMITTEE MINUTES

The Advisory Committee met at the Hotel Tast, New Haven, Connecticut, at 10.30 A.M., Monday, April 2, 1923, with President Franklin in the Chair and Messrs. H. E. Howe, A. B. Lamb, Wm. McPherson, W. A. Noyes, Edgar F. Smith, and Charles L. Parsons present,

A communication was read from the National Conference on Pharmaceutical Research, requesting the American Chemical Society to appoint a delegate or "unofficial observer" to the Asheville meeting of this Conference to be held in Asheville, N. C., September 1, 1923. The President, with the advice of the Committee, appointed Oliver Kamm as the delegate to this meeting.

A communication was received from A. H. Nuckolls of the Underwriters' Laboratories, transmitting the request of George W. Booth, Chief Engineer, National Board of Fire Underwriters, and Chairman of the National Fire Protection Association Committee on Hazardous Chemicals and Explosives, requesting the coöperation and assistance from the American Chemical Society and the appointment of a committee to assist in this work. After careful consideration, the President, with the advice of the Committee, appointed a committee to consist of Charles E. Munroe, H. LeB. Gray, A. H. Nuckolls, James A. Rafferty, Fred C. Zeisberg.

President Franklin, with the advice of the Committee, appointed W. D. Bigelow, H. P. Cady, and F. J. Moore to represent the American Chemical Society in the Division of Chemistry and Chemical Technology of the National Research Council for the term ending 1926.

A communication was received from the Societe D'Encouragement Pour l'Industrie Nationale requesting the appointment of a delegate to their convention in Paris from the 7th to the 10th of June, 1923. The President himself being unable to attend, with the advice of the Committee, he appointed Professor R. E. Swain of the University of California as the delegate of the Society thereto.

A letter to the Secretary from the Secretary of the American Engineering Standards Committee, dated March 27th, regarding the question of abbreviations and symbols, was presented to the Advisory Committee. The Committee was of the opinion that it will be quite impossible for the American Chemical Society to effectively coöperate on chemical abbreviations and symbols with others than international chemical and physical societies and instructed the Secretary to inform Mr. Agnew that while we wish in every way to be helpful, the Committee felt that the matter of chemical abbreviations and symbols was a question for the chemical societies of the world, but that they were ready to be of assistance at any time and would communicate with his Committee concerning the results that have been obtained by many years of careful study of these specifically chemical matters.

The Committee voted to recommend to the Council that certain letters in the possession of the Secretary, such as the acceptances of Honorary Membership, be donated to the collection of Edgar F. Smith for proper preservation.

A communication from W. D. Collins was presented to the Advisory Committee regarding the use of names of certain manufacturers that he had used in his report. The Committee expressed its opinion that there was no reason why these names should not be included in his report.

## ADVISORY COMMITTEE MEETING

## April 3, 1923

The Committee met in Byers Hall on Tuesday afternoon, April 3, 1923, at 5.30 P.M., with E. C. Franklin in the Chair, and Messrs. Comey, Howe, McPherson, Noyes and Parsons present.

The Committee voted to call an additional Council meeting on the afternoon of Wednesday, permission having been obtained from the officials of Yale University to thus infringe upon their program.

The Committee voted to recommend to the Council that the Monday preceding the opening of general meetings be kept free for Council business and that no complimentary dinner to members of the Council be held in future.

A request was received from the Federated American Engineering Societies for the appointment of a delegate to a Committee on Coal Storage. The President with the advice of the Committee, appointed S. W. Parr thereto.

#### ADVISORY COMMITTEE MEETING

# April 5, 1923

A meeting of the Advisory Committee was held at the Graduate Club, Yale University, Thursday noon, April 5, 1923, with E. C. Franklin in the Chair and Messrs. H. E. Howe, W. A. Noyes, Edgar F. Smith, and Charles L. Parsons present.

The question of geographical distribution of Directors, the question of personnel of an Executive Committee, and the question of changes in Council representation, referred to it by the Council were discussed freely. The Secretary was instructed to formulate the views of those present, to present them to the other members of the Advisory Committee, and to have them in form for final approval of the Advisory Committee and presentation to the Council at the Milwaukee meeting.

As directed by the Council, President Franklin, with the advice of his Committee, appointed M. T. Bogert, Chairman, W. Lee Lewis, R. W. Neff, O. F. Stafford, and C. E. Coates a special Committee to consider the subject of inter-sectional meetings and all its bearings and to formulate a working plan to be submitted to the Council for consideration at its next meeting.

By direction of the Council, President Franklin, with the advice of the Committee, appointed Wm. Hoskins, Chairman, A. D. Little, and James Kendall a Committee to consider the whole matter enhancing the value placed on membership and to make special recommendations to the Council for final action at the Milwaukee meeting.

The Committee then adjourned. Charles L. Parsons, Secretary

# COUNCIL MINUTES

The Council of the American Chemical Society met in Byers Hall, Yale University, New Haven, Connecticut, on April 2, 1923, at 2.30 p.m., with President E. C. Franklin in the Chair and the following Councilors present:

Ex-Officio.—Wilder D. Bancroft, Marston T. Bogert, A. M. Buswell, E. J. Crane, G. J. Esselen, Jr., Charles H. Herty, W. F. Hillebrand, William Hoskins, J. S. Hughes, Arthur B. Lamb, A. D. Little, Arthur A. Noyes, H. A. Noyes, W. A. Noyes, Charles L. Parsons, Edgar F. Smith, John E. Teeple, John Arthur Wilson, Robert E. Wilson.

Councilors-at-Large.—Roger Adams, C. L. Alsberg, A. M. Comey, H. E. Howe, Lauder W. Jones,

Councilors-at-Large.—Roger Adams, C. L. Alsberg, A. M. Comey, H. E. Howe, Lauder W. Jones, Wm. McPherson, Allen Rogers.

Local Sections.—Akron, R. P. Dinsmore, W. J. Kelly (subs. for H. E. Simmons). Ames, W. F. Coover. California, C. W. Porter (subs. for J. H. Hildebrand). Central Texas, J. R. Bailey. Chicago, D. K. French (subs. for W. R. Smith), Herbert N. McCoy, Carl S. Miner (subs. for Paul Van Cleef), A. V. H. Mory (subs. for L. M. Tolman), L. V. Redman, Ethel M. Terry, G. L. Wendt, Frank C. Whitmore. Cincinnati, A. B. Davis, C. P. Long, H. J. Morrison. Clearland, L. C. Drefahl, Hippolyte Gruener (subs. for W. R. Veazey), A. W. Smith, O. F. Tower. Colorado, W. D. Engle. Columbus, E. C. Hytree (subs. for Wm. L. Evans). Connecticul Valley, Joseph S. Chamberlain, C. R. Hoover. Cornell, A. W. Browne. Delaware, Charles L. Reese, Charles M. Stine. Detroit, W. P. Putnam. Indiana, Fred C. Atkinson, Horace A. Shonle (subs. for H. W. Rhodehamel). Iowa, Edward Bartow. Kansas City, H. M. Elsey (subs. for R. Hirsch), H. H. King (subs. for F. B. Dains). Lehigh Valley, John T. Little. Louisiana, C. E. Coates. Louisville, A. W. Homberger. Maryland, A. A. Backhaus, N. E. Gordon, A. E. Marshall. Midland, William J. Hale. Minnesota, Paul H. M.-P. Brinton (subs. for C. A. Mann), L. M. Henderson (subs. for R. A. Gortner). Maine, C. A. Brautlecht (subs. for A. B. Larcher). Milwaukee, T. Harry Cochrane (subs. for C. R. McKee). Nebraska, Fred W. Upson. New Haven, H. W. Foote. New York. Clarke E. Davis, Thomas B. Fress (subs. for James Kendall), F. H. Getman, Ellwood Hendrick, William Haynes, Martin H. Ittner, D. B. Keyes (subs. for B. T. Brooks), D. H. Killeffer (subs. for C. A. Browne), Sidney D. Kirkpatrick (subs. for R. G. Wright), A. C. Langmuir, K. G. MacKenzie, H. C. Parmelee, R. R. Renshaw (subs. for H. G. Sidebottom), Arthur S. Thatcher (subs. for D. W. Jayne), Arthur W. Thomas, B. R. Tunison, F. M. Turner, Jr., (subs. for H. R. Moody), David Wesson, Lois W. Woodford. North Carolina, Paul W. Gross. Northeastern, George L.

Stuart J. Bates. St. Louis, A. C. Boylston, Chas. W. Cuno. Syracuse, R. S. Fleming, Louis E. Wise, University of Illinois, B. S. Hopkins, H. C. Kremers (subs. for S. W. Parr). University of Michigan, H. H. Willard. University of Missouri, C. Robert Moulton (subs. for H. D. Hooker, Jr.). Vermont, S. Francis Howard. Virginia, W. F. Rudd, Garnett Ryland. Washington, D. C., W. D. Bigelow (subs. for R. B. Sosmanl, W. D. Collins, F. C. Cook (subs. for R. C. Wells), W. W. Skinner. Western New York, M. J. Ahern (subs. for A. M. Williamson), Walter Wallace. Wisconsin, L. F. Hawley, Victor Lenher.

On recommendation of the Advisory Committee, the Secretary was instructed to present to Edgar F. Smith, for his historical collection and future preservation, autograph letters in his possession, from prominent chemists especially such acceptances of Honorary Membership as are in the Society's files.

The following resolutions were passed on our Honorary Member, Edward Williams Morley, recently deceased, the Council remaining standing in silence for a few moments in memory of our beloved and honored colleague.

#### EDWARD WILLIAMS MORLEY

The American Chemical Society in this memorial wishes to express its appreciation of the great loss it has sustained by the death of Professor Edward W. Morley, who was to have been the Honorary

Chairman of this meeting.

Born in 1838, graduated from Williams College in 1860, he entered the Congregational ministry and was called from it to be Professor of Natural History and Chemistry in Western Reserve College in 1869. He was actively connected with this institution for 37 years and since his retirement has made his home near Hartford, Connecticut, in which city he died on February 24th of this year, shortly after

his home near Hartford, Connecticut, in which city he died of reprilary 24th of this year, shortly after his 85th birthday.

Although Western Reserve College was but little known at that time, Professor Morley soon brought it into prominence and raised himself by his own genius to be one of the foremost scientists of his time. He was as much a physicist as a chemist, and most of his published papers, curiously enough, lie in the domain of physics, although he allied himself primarily with the chemists.

With remarkable characteristics for precision and thoroughness, he possessed also an unusually clear and resourceful mind and a wonderful mechanical skill, so that he was not only a great investigator

but also an inventor of many new devices for fine and exact measurement. Among these were a prebut also an inventor of many new devices to the anti-exact measurement. Among these were a precision endiometer for the rapid determination of oxygen, two types of differential manometers, by which differences of gaseous pressure can be measured to the 1/10000 mm, of mercury, and many mechanical features of a minor sort used in the manipulation of gases. Together with Professor Michelson he developed the interferometer, an apparatus for measuring lengths in terms of the wave-length of light, and employed it in measuring the expansion of measuring lengths in terms of the wave-length of fight, and the velocity of light in a magnetic field.

The work, however, for which he is best known among chemists, is that on the densities of oxygen

and hydrogen and the ratio in which they combine, published as Smithsonian Contribution to Knowledge, No. 980. This research, finished in 1895 and on which he was engaged for eleven years, brought

him world wide recognition as a scientist of the first rank.

Professor Morley was of a very modest and retiring nature, never pushing himself forward, and for this reason he was not known intimately to many. But those few, who enjoyed the privilege of knowing him well, were impressed by the sweetness of his nature, the broadness of his culture and knowledge, the nobleness of his spirit and the wisdom of his counsel.

By making him its President in 1899 and electing him to honorary membership in 1900 this

Society honored not so much him as itself,

It was voted to grant a charter for a new local section to be known as the Erie Section with territory comprising Erie and Crawford Counties, Pennsylvania, and with headquarters at Erie.

It was voted that when the Constitutional requirements have been met the President and Secretary be authorized to issue a charter for the formation of a local section covering the counties adjacent to Rock Island and Moline, Illinois, and Davenport and Clinton, Iowa, to which waivers of jurisdiction have been received from the Iowa, the Chicago, and the University of Illinois Sections, and for which a request in Constitutional form has not vet been received.

A. M. Comey was elected successor to George D. Rosengarten on the Committee on National Policy for the ensuing two years.

A motion by C. E. Davis to reverse the action of the Advisory Committee as taken on May 13, 1922, on the Stanley Bill, was defeated.

The report of the Committee on Progress in Society Procedure was then received. After somewhat lengthy discussion, which was, unfortunately interfered with by the necessity of adjournment for the Council dinner, the whole report was referred to the Advisory Committee to consider and to report to the local sections, and to finally report at the meeting of the Society in Milwaukee.

Committees reported as follows:

Committee advisory to the Bureau of Mines and Bureau of Standards on non-ferrous metals -The committee reported a list of the subjects discussed at meetings at the Bureau of Standards on April 24 and October 31 and at the Bureau of Mines on April 25 and November 1, but mentions no definite conclusions arrived at.

Committee advisory to the War Department.—The committee reported that during the year it had discussed with the Assistant Secretary of War and officers of the War Department the question of the dyes to be used in the dyeing of uniforms and the question of a special color or mixture of colors

of the dyes to be used in the dyeing of uniforms and the question of a special color of mixture of colors to be used in uniforms which would be as invisible as possible when viewed through color screens,

**Committee in coöperation with Chemical Warfare Service,**—The committee reported close cooperation with the Chemical Warfare Service, including visits to Edgewood Arsenal and the study of 
reports submitted by the individual members of the staff.

Committee to consider question of a non-society employment Bureau.—The committee reported close canvass of the local sections with reference to the adoption of an employment service in copperation with the local sections and found very diverse sentiments. After careful consideration, they recommended to the Directors that a budget of \$2,100.00 be voted to print a maximum of four additional pages in each issue of the News Edition of Industrial and Engineering Chemistry to be devoted to employment information.

Committee on cooperation between industries and universities.—The committee reported progress

but no specific accomplishments during the year.

Committee on Endowment.—The committee reported that no funds had been added to the Society's endowment during the year.

Committee on Exchange.—The committee reported as follows:

The Society now has 434 exchanges. Of these 37 are new since our 1922 report. Fifteen exchanges have been discontinued and 5 old exchanges, previously discontinued for one reason or another, have been resumed. Ten exchange proposals to us have been refused and 3 of our requests have not been granted. Of the journals received by exchange 43 go to the office of Industrial and Engineering Chemistry, 3 to abstractors for Chemical Abstracts and the remainder to the office of Chemical Abstracts.

Exchanges are approved by the Committee only in case it is believed that the Society will benefit thereby. They save the Society a good deal of subscription money which would otherwise have to be paid out in the office of Industrial and Engineering Chemistry or in that of Chemical Abstracts. If a needed journal can be obtained more cheaply by subscription than by exchange, it is the practice to subscribe.

E. J. Crane, H. E. Howe, A. B. Lamb, Committee

Committee on Finance.—The committee reported as follows:

The Finance Committee begs to report that for the year 1922 the Society paid its own way and ended the year with a small surplus of income over expenditures. Details may be seen in the Auditors'

Report and Treasurer's Report already published.

The only changes that have taken place in the permanent investment of the funds during last year are the maturity of \$10,000 in Victory Bonds and the purchase of \$10,000 Third Liberty Bonds to

year are the maturity of \$10,000 in victory bonds and the putchase of \$10,000 kind 2000, year has been invested in Liberty Bonds. The uninvested residue of the Life Membership Fund, amounting to about \$600, has been invested in Liberty Bonds.

The various Trust Funds of the Society are in proper shape.

Attention should be called to the fact that the Life Membership Fund is not increasing. The

income from the invested fund, in fact, is not sufficient to pay the annual dues of the existing life mem-It was intended that this Fund should grow into a research fund but its growth will be exceedingly slow at the present rate.

John E. Teeple, Chairman F. J. Metzger F. G. Zinsser

Committee on Guaranteed Reagents and Standard Apparatus.—This report is printed in full in Industrial and Engineering Chemistry for May.

Committee on Importation of Foreign Books (To consider question of).—The committee reported

as follows:
Your Committee appointed to consider the question of importation of foreign books would sub-

mit the following report.

Assuming that the 'foreign books' referred to were books and periodicals sold in Germany to Americans, this is the only phase of the subject which has been studied.

Price lists have been studied, correspondence has been had with German booksellers, and a letter was addressed to Dr. F. Haber, the president of the Deutschen Chemischen Gesellschaft, copies of which were also sent to a number of booksellers and others for comment. (Copy of the letter to Dr. Haber

and his reply are appended to this report.)

It appears that during the past year the prices to Americans for German books and periodicals have been based on pre-war prices, with more or less advance; but that to nationals the prices remained the same or with slight advances until some three or four months ago, since which time they advanced very rapidly. For example, the price of the Chemisches Zentralblatt has advanced from 1000 marks in October last to 84,000 marks two weeks ago. This advance has undoubtedly been occasioned by the criticism in England and the United States. Before the German prices began to rise the cost to na-

crucism in Engiand and the United States. Before the German prices began to rise the cost to nationals was very low in terms of American money, and naturally gave rise to a multitude of complaints.

As regards the publications of the Deutschen Chemischen Gesellschaft, the letter of Dr. Haber seems to make it clear that their policy is based primarily, not on cost but upon the supposed value of the publication to the subscriber, in proportion to his means; this would seem to be rather a socialistic

standpoint.

From other sources it would appear that much of the chemical material published in Germany today is sold to nationals below the actual cost of publication, in order that the science may not suffer while to non-nationals prices are fixed on approximately the pre-war basis, augmented by the generally increased cost of all commodities. This does, of course, make up to a greater or less extent for the losses

incurred in sales to nationals.

The disparity between actual costs to nationals and non-nationals is rapidly growing less, probably owing to criticism and fear of diminishing sales to non-nationals. The present method of fixing prices appears to be somewhat as follows—first placing a Grundzahl for each publication. This seems to be a number representing the cost in marks before the war, augmented by an increase of say 50%

to 100%. This is multiplied by a Schlüssel-(key)zahl which is fixed by the Börsenverein of German booksellers, and varies with current exchange. This Schlüsselzahl seems to be about half the number of marks purchasable by a Swiss franc. These two figures multiplied together give the cost of the publication in marks, and this price will be in general somewhere about half the price quoted in dollars. If this system is fairly carried out, without rebate to nationals, no inconsiderable part of the cause of

If this system is fairly carried out, without rebate to nationals, no inconsiderable part of the cause of complaint will have been done away with.

Regarding second-hand books and files of journals, none of the restrictions of the Börsenverein apply and each dealer is free to make his own prices. Many of the quotations are made in dollars and at pre-war prices, and at these figures enormous profits must be made, but there are dealers who quote prices which are in keeping with the costs of the books to them. We can only advise against the purchase of books where the price appears too high.

Inasmuch as the Germans seem to be taking the matter of American and English criticism very with the most of the continued at least until the Fall.

seriously, we would suggest that this, or a similar committee, be continued, at least until the Fall meeting of the Society.

Respectfully submitted,

JAS. Lewis Howe, Chairman Walter Taggart R. A. GORTNER E. EMMET REID

Committee on Industrial Alcohol .- This report will be found in full in the May issue of Industrial Engineering Chemistry.

Committee on Institute for Chemo-Medical Research.—The committee reported as follows:

On behalf of the Committee on An Institute for Chemo-Medical Research I beg to say that during the year no formal meetings of the Committee have been held.

A large amount of interesting correspondence has been received covering all classes and pro-

fessions in all parts of the country, expressing deep interest in the subject covered by the Report published last year by the Chemical Foundation, and distributed to the extent of nearly a million copies. It has been particularly interesting to note how strongly the report has appealed to lawyers, a large number of whom have written words of appreciation.

number of whom have written words of appreciation.

While no funds have yet been donated which could be used for carrying out the main purpose of the Report, nevertheless it is believed that the Report has been influential in increasing cooperation between chemists, pharmacologists and biologists in the solution of problems in this important field, and it is recommended that the Committee be continued.

Respectfully submitted for the Committee,

Chas. H. Herry, Chairman

Committee on Membership.—The committee reported as follows:

Individual Members elected 1922	1, 576
Members Resigned 1922 Deceased Members 1922	
Total membership at end of year 1922	14, 400
Members dropped for delinquency January 1, 1923	1.278

W. D. BIGELOW, Chairman F. G. COTTRELL Chas. L. PARSONS

Committee on Metric System.—The committee reported as follows:

The Metric Committee reports that during the year we have published several articles in the magazines; we have procured a large number of memberships for the Metric Association; we have conducted a successful metric conference between the various scientific societies at Pittsburgh obtaining from Dr. Mendenhall an important contribution to the literature of the subject which has been published in Science; we have secured the promise of additional universities and corporations to purchase their supplies according to metric specifications; and we have carried on a considerable correspondence in regard to metric matters. EUGENE C. BINGHAM, Chairman

Committee on Nomenclature, Spelling and Pronunciation.—The committee reported as follows: Your Committee on Nomenclature, Spelling and Pronunciation respectfully submits the fol-

lowing annual report.

In the July, 1922, number of the Journal of the American Chemical Society (Proceedings, pages 77-8) the committee has published as tentative for one year a list of nomenclature rules covering the more important points concerning which there are more or less common differences in practice. These rules were worked out with the cooperation of a corresponding committee of the London Chemical Society. Criticism of them has been invited but none has been received thus far.

Copies of these rules, together with a letter urging coöperation in their application, have been sent to the editors of 49 American journals publishing chemical articles.

In view of the appointment of a number of national and international committees on nomen-

clature by the International Union of Pure and Applied Chemistry, it has seemed best for your committee, for the present at least, to leave the initiative in further nomenclature developments to these active committees, for international standards are of course better than national ones. A readiness to cooperate with the International Union committees has been expressed. Several members of your

committee (Norris, Noyes, Patterson and Crane) are on one or more of the American or International committees of the International Union.

The most important development during the past year in the field of our interest as a committee has been the working out by Dr. Austin M. Patterson of a comprehensive set of rules for numbering organic ring complexes. There is great need for reform and standardization in this domain. The rules are now being considered by the American Committee on Organic Nomenclature of the International

Union.

The chairman of your committee has received an increasingly large number of requests for information or advice on nomenclature matters. An effort has always been made to help.

E. J. Crane, Chairman

Committee on Occupational Diseases in Chemical Trades.—This report will be found in full in the May issue of Industrial & Engineering Chemistry.

Committee on Paper.—The committee reported in detail the quality of paper used in the journals of the Society and in their covers, showing the quality of the paper in the journals to be approximately the same as last year and the quality of the cover paper on the whole improved. The committee recommends that as financial conditions permit the quality of the paper should be made to consist of at least 50% of a good grade of rag and be restored to its prewar quality.

Committee on Patent and Related Legislation.-The committee reported as follows

Your Committee takes pleasure in reporting that the Sterling-Lehlbach bill, H.R. 8928, providing for the reclassification of certain governmental salaries, including those of Patent Examiners, became a law on March 4, 1923. This bill, which has received the active support of the American Chemical Society, increases the salaries of the Primary Examiners to \$5000, and provides generally for increased salaries in the scientific bureaus of the Government. So far as the Patent Office is concerned, it is our hope and expectation that this will result eventually in placing the work of that Department upon an appreciably higher plane. The passage of this bill however marks only the beginning of our endeavor.

The American patent system is based upon the proposition that the matter submitted for patenting shall be subjected, before grant of the patent, first, to an adequate examination as to its novelty; and second, to a careful review as regards the existence of a meritorious invention. Both of these and second, to a careful review as regards the existence of a meritorious invention. Both of these questions are passed upon by the patent examiners. Of the two questions, the first is essentially technical and the second essentially judicial: and therefore the competent examiner must possess a combination of qualities not to be acquired by any formal schooling. Proper examination of a patent application is a work in which long experience, an intimate acquaintance with the art, and a wide familiarity with the attitude of the Federal Courts in patent cases are required; and it is clear that these qualifications cannot exist in an xamining corps subject to a heavy turn-over in its personnel or consisting largely of young men fresh form the technical schools. Yet this is the condition which the Patent Office has encountered in ever increasing intensity during recent years, and which we hope the enactment of the new legislation will remedy, at least in a measure. But it cannot be emphasized too strongly that this legislation is only a step; that we have been facing and are still facing an actual breakdown of our examining system under the double burden of an inexperienced examining corps and an ever increasing accumulation of patents and technical literature affecting the validity of new patents; and that unless Congress can be induced to assume and maintain a liberal attitude toward our patent system its eventual collapse is inevitable.

The Patent Office divisions are now months and in some cases years behind in their examination

of applications. Every progressive manufacturer is liable to be adversely affected by this delay, which prevents the prompt commercialization of new inventions. This situation is not remedied but only aggravated by any feverish haste in the disposal of pending applications, such haste often resulting in the grant of ill-considered, inadequately searched and consequently invalid patents, which may nevertheless stand for years as obstacles in the path of real progress. It can be remedied only by the provision of a Patent Office personnel adequate to the work in hand; and for the enlightened leadership which will eventually give us such an establishment we must look to the great scientific, engineering and manufacturing associations of the country.

C. P. TOWNSEND, Chairman

Committee on Preparation and Publication of a List of Ring Systems Used in Organic Chemistry.

The committee reported progress and asked to be continued.

Committee on Revision of Melhods of Coal Sampling and Analysis (Joint with the Society for Testing Materials).—The committee reported some progress during the year in the methods of testing the fusibility of coal ash which they hope to present shortly to the Supervisory Committee of the American Chemical Society.

Committee on Standard Methods for the Examination of Water and Sewage to Coöperate with Committee of American Public Health Association.—The committee reported as follows.

As Chairman of the Committee on Standard Methods for the Examination of Water and Sewage of the American Chemical Society I wish to submit the following report:

As stated in the report of this Committee submitted March 17, 1922, the manuscript for chemical methods of water examination was completed in collaboration with the Committee of the American Public Health Association. The printing of Standard Methods is nearly completed, the entire galley proof having been corrected. When printed it is the intention of this Committee to submit a copy to the President of the Society as record of its activities to date.

A. M. Buswell, Chairman

Committee on Standardized Methods for Vitamin Research.—The committee reported progress, mendations having been received by correspondence. The committee expects to meet at the New recommendations having been received by correspondence. Haven Meeting.

Committee on Supervision of Chemical Engineering Catalog.—Did not report.
Supervisory Committee on Standard Methods of Analysis.—The committee reported as follows:
In accordance with the provisions of the constitution relating to committees of the Society,
I have to report as follows for the period that has elapsed since my last report of March 9, 1922.
The Committee on Methods of Analysis and Specifications of Commercial Soaps and Soap
Products of the Division of Industrial Chemists and Chemical Engineers submitted a report on Stand-

and Methods for the Sampling and Analysis of Commercial Soaps and Soap Products which was formally approved by the committee of which I am chairman and was printed in Journal of Industrial and Engineering Chemistry, Vol. 14, pp. 1159-63, 1922.

A report from the Committee on Fats and Oils of the Division of Industrial Chemists and Chem-

ical Engineers is now under consideration.

Respectfully submitted, W. F. Hillebrand, Chairman

The Council then adjourned.

# COUNCIL MEETING

## April 4, 1923

A second meeting of the Council was called by President Franklin on the advice of the Advisory Committee for Wednesday afternoon, April 4, 1923, at 3 o'clock. The Council was in session until half past seven, giving every Councilor full opportunity to consider the important report of the committee on Progress in Society Procedure. President Franklin was in the Chair and the following Councilors were present:

Ex-Officio.—Wilder D. Bancroft, Marston T. Bogert, Edgar B. Carter, E. J. Crane, G. J. Esselen, Jr., Charles H. Herty, W. F. Hillebrand, William Hoskins, Wm. H. Nichols, Arthur A. Noyes, H. A. Noyes, W. A. Noyes, Charles L. Parsons, Edgar F. Smith, H. W. Wiley, John Arthur Wilson, Robert E. Wilson.

Councilors-at-Large.—Roger Adams, C. L. Alsberg, A. M. Comey, H. E. Howe, Lauder W. Jones, Wm. McPherson.

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Local Sections.—Akron, R. P. Dinsmore, W. J. Kelly (subs. for H. E. Simmons). Ames, W. F. Coover. Arkansas, J. W. Read (subs. for Harrison Hale). California, C. W. Porter (subs. for J. H. Hildebrand). Central Texas, J. R. Bailey. Chicago, D. K. French (subs. for W. R. Smith), L. V. Redman, Ethel M. Terry, G. L. Wendt, Frank C. Whitmore, Cincinnati, C. P. Long, H. J. Morrison. Cleveland, L. C. Drefahl, Hippolyte Gruener (subs. for W. R. Veazey), O. F. Tower. Colorado, W. D. Engle. Connecticut Valley, Joseph S. Chamberlin, C. R. Hoover. Cornell, A. W. Browne. Delaware, Charles L. Reese, Charles M. Stine. Detroit, W. P. Putnam. Indiana, Fred C. Atkinson, Horace A, Shonle (subs. for H. W. Rhodehamel). Iowa, Edward Bartow. Kansas City, H. M. Elsey (subs. for R. Hirsch). Lehigh Valley, John T. Little. Louisiana, C. E. Coates. Maryland, A. A. Backhaus, N. E. Gordon, A. E. Marshall, Minnesota, Paul H. M.-P. Brinton (subs. for C. A. Mann), L. M. Henderson (subs. for R. A. Gortner). Maine, C. A. Brautlecht (subs. for A. B. Larcher). Milwankee, T. Harry Cochrane (subs. for C. R. McKee). Nebraska, Fred W. Upson. New York, Clarke E, Davis, Thomas B. Freas (subs. for Martin H. Ittner), Sidney D. Kirkpatrick (subs. for R. G. Wright), K. G. MacKenzie, R. R. Renshaw (subs. for H. G. Sidebottom), Arthur W. Thomas, David Wesson, Lois W. Woodford. Norlheastern, J. B. Conant, George L. Coyle, George Defren, Winthrop C. Durfee, W. L. Jennings, Herman C. Lythgoe (subs. for G. S. Forbes), Robert W. Neff, J. F. Norris, L. A. Praett. Northern Indiana, J. A. Nieuwland. Oklahoma, Edwin DeBarr. Philadelphia, G. E. Barton, C. S. Brinton (subs. for H. S. Miner) J. S. Coldbaum. Edwin F. Hicks, George Defren, Winthrop C. Durfee, W. L. Jennings, Herman C. Lythgoe (subs. for G. S. Forbes), Robert W. Neff, J. F. Norris, L. A. Praet. Northern Indiana, J. A. Nieuwland. Oklahoma, Edwin DeBarr. Philadelphia, G. E. Barton, C. S. Brinton (subs. fo

A motion was first made to reconsider the reference of this report to the Advisory Committee and to place it before the meeting. It was then voted that the Council go into a committee of the whole and in committee of the whole the report was discussed. section by section, for nearly four hours. The Committee then rose and reported to the Council, the various sections of the report being acted upon as follows:

The following section was referred to the Advisory Committee with instructions to formulate a general plan of regional representation in the directorate, with the recommendation that by-laws be made to provide for reimbursement of expenses of directors incurred in attending meetings of the board other than those held at the time of general meetings, and to report at the Milwaukee meeting.

# GEOGRAPHICAL DISTRIBUTION OF DIRECTORS

The Committee believes that some form of equitable, regional representation on the Society's Board of Directors is especially to be desired, since the closer touch thus insured cannot fail to be in the interest of harmony and cooperation.

The Committee has in mind a plan of dividing the whole country into districts, six in number, each to have its own representative on the Board to be nominated and elected within the district represented. In determining boundaries for the proposed districts the Committee counsels a compromise

between a strictly membership and a strictly geographical division.

The Committee therefore recommends that the Council approve the general plan of regional representation of Directors and appoint a committee to determine territorial boundaries that will afford equitable representation, and to propose such changes in the Constitution and By-Laws as may be necessary under such a plan, its findings to be reported to the Council for final action at an early date.

In the event of the adoption of such a plan, the Committee recommends that the By-Laws be made to provide for reimbursement of the Directors for expense incurred in attending meetings of the Board.

The following section of the report was referred to the Advisory Committee to report their recommendation at the Milwaukee meeting, with the recommendation that there be three elected members of the Executive Committee and only one past-president, and that the Executive Committee be given full powers of the present Advisory Committee, and, further, that they be given the usual functions of an Executive Committee.

## THE ADVISORY COMMITTEE

The Committee originally characterized, by both name and function, as the Committee on National Policy, has become in effect since war times an Executive Committee of the Council. As such it should be continued and so employed as to increase the efficiency of the body it serves. Change of function suggests possible advantage in change of personnel. As providing more direct representation of the Council, the Committee recommends that one additional member elected from the Councolors at Large be substituted for the earlier of the two Past Presidents, that the name of the committee be changed from the Committee on National Policy to the Executive Committee of the Council. and

be changed from the Committee on National Policy to the Executive Committee of the Council, and that this committee be provided for in the By-Laws as follows:

ARTICLE XIII—3 (a). There shall be an Executive Committee of the Council consisting of the last Past President, the Editor of the Journal of the American Chemical Society, the Editor of Industrial & Engineering Chemistry, the Secretary, and three Councilors at Large, one to be elected each year for a term of three years by the Council at the annual meeting.

(b) The Executive Committee of the Council shall serve in an advisory capacity in connection with all matters of importance coming before the Council, and, when the Council is not in session, shall cooperate with the Board of Directors in handling matters which may properly come before the Council, but which in the discretion of the Directors do not call for letter ballot of the Council.

The following section was referred to the Advisory Committee, to report at the Milwaukee meeting, with the recommendation that in some way the Council be reduced in size.

#### THE COUNCIL

Closely related to the matter of making our Board of Directors a more directly representative body is that of correcting the relative inefficiency now generally admitted as characterizing our representative body, the Council. The Committee believes the Council has grown to be too large for the effective transaction of the Society's business, and, as a first step in the interest of better efficiency, favors a reduction in the number of Councilors. It is therefore recommended that the Constitution be made to provide for one representative for each two hundred members of the Society in full standing.

be made to provide for one representative for each two hundred members of the Society in full standing, or fraction thereof, instead of for each one hundred as at present, and that the Constitution be revised in accordance with this plan to read as follows:

"ARTICLE IV—Section 3. The Council shall consist of the President, the Past Presidents, the Secretary, the Treasurer, the Editors, and the Chairmen of the Divisions ex-officies, one representative elected by each Local Section for each two hundred members of the Society in full standing, or fraction thereof it may have, and twelve members elected at large, one-third of the last named being chosen each year."

The recommendation of the Committee on Progress in Society Procedure covering Article 13, Section 4, of the Constitution, regarding meetings of the Council, was laid on the table, and instead thereof the Council, on recommendation of the Advisory Committee, voted that the Monday preceding the opening of general meetings be confined to Council business and to that end no complimentary dinner to the Council be held.

It was voted that a special committee be appointed to consider the following paragraph of the report of the Committee on Progress in Society Procedure and to report at the Milwaukee meeting.

## INTERSECTIONAL MEETINGS

At Birmingham, the Council went on record as favoring Intersectional Meetings, but did not

undertake to specify the exact character of such meetings.

The Committee finds much difference of opinion among the Sections concerning the matter of whether or not Intersectional Meetings should be given the status of, and replace one of the National Society's meetings. But, while there is much difference of opinion concerning details, there plainly is a growing interest in the Intersectional Meeting as a national institution. Its merits can scarcely be

judged, however, until an attempt has been made to work out a plan in detail.

Accordingly, it is recommended that a special committee be appointed to study the subject of Intersectional Meetings in all its bearings and to formulate a working plan to be submitted to the Council for con-

sideration at its next meeting.

President Franklin appointed the following committee: M. T. Bogert, Chairman, W. Lee Lewis, R. W. Neff, O. F. Stafford, and C. E. Coates.

It was voted that the following section of the report of the Committee on Progress in Society Procedure be referred to a special committee to report at the Milwaukee meeting:

## METHOD OF ELECTION OF MEMBERS AND CLASSIFIED MEMBERSHIP

The suggestion has been made that membership would be more highly prized, as well as better safeguarded, were it required that all nominations bear the signatures of Local Section officers. This, however, is met by the objection that many prospective and desirable members have little or no contact with, and are unknown in Local Sections. The present requirement, by which the candidate must be nominated by three members of the Society in good standing, appears to the Committee to be reasonably adequate, since under its operation the Society has suffered to almost a negligible extent from undesirable members. The Committee has no recommendation to make, therefore, for further safeguarding membership under present eligibility requirements.

On the other hand, there appears to be a growing sentiment in favor of taking some step in the direction of causing membership in the Society to be more highly prized.

Those who favor some form of classification of membership insist that pride in membership would thus be enhanced and a stronger professional spirit be developed among our members. Others fear that any form of classification of members would tend to destroy the democratic spirit of the So-

All agree, however, that a strong desire to aid in the advancement of chemistry and the promotion of chemical research should impel every chemist in America to seek membership in the Society that is doing so much for the cause of chemistry. No other incentive should be needed, and yet we find even our most loyal members either criticizing or defending the present cost of membership altogether in terms of the value of the Society's publications. We learn that, of the National Engineering Societies, none has a cost of membership so low as ours, nor publications so rich and extensive. But membership in the Engineering Societies implies some degree of proficiency in engineering. Does this fact cause membership to be more highly prized so that publications are thought of as merely incidental to membership? Those who favor some form of classified membership believe it does, and ask: "May not the time have come for return to the policy of requiring that full membership in the American Chemical Society shall imply some reasonable degree of proficiency, as well as interest, in chemistry?" The question also arises: What other measures are there worth considering for their possible value in stimulating pride in membership and a stronger professional spirit in the Society?

Your Committee is prepared only to raise these questions, but, feeling that the answer is of great importance to the welfare of the Society, strongly recommends that a special committee be appointed charged with studying this whole matter of enhancing the value placed on membership and be instructed to report its findings, with specific recommendation, to the Council for final action at its next meeting.

The President appointed the following Committee: Wm. Hoskins, Chairman. A. D. Little, and Tames Kendall.

The balance of the report of the Committee, reading as follows, was unanimously adopted by the Council:

The foregoing deals with the original, and related, problems specifically named in the authorization of our Committee given by vote of the Council at Birmingham.

At Pittsburgh the Committee was further instructed to take under advisement any other matters that might be brought to its attention by the Local Sections. A considerable number of Sections responded offering criticism and comment, all of which has been given careful consideration by the Committee, which desires to make further report as follows:

#### FINANCES

A number of the Sections asked that the Committee learn the facts concerning the Society's financial condition. Feeling that all of the points raised by the Sections should be cleared up without nnancial condition. Feeling that all of the points raised by the Sections should be cleared up without delay, the Committee, at the time of its session in Washington, January 3rd and 4th last, made a request that a special report be prepared by the Secretary and published in the News Edition of Industrial & Engineering Chemistry giving a full and clear statement of the facts concerning the conduct of the Society's business. This report, which appeared on January 20th, indicates that the present financial condition of the Society is sound, and that comparison with the National Engineering Societies of the country is distinctly favorable to the American Chemical Society in both cost of membership and tangible returns for money expended.

OFFICE OF THE SECRETARY AND OF THE EDITOR OF Industrial & Engineering Chemistry

It has been suggested that there would be advantage in bringing together the office of the Secretary and the office of Industrial & Engineering Chemistry.

Inspection of these two offices by the Committee, during its recent session in Washington, showed little or no duplication of clerical work and no excess of floor space in either office. Simply bringing the two offices together under one roof, therefore, gives little or no promise of important saving

two offices together under one roof, therefore, gives little or no promise of important saving. In considering the desirability of effecting whatever saving might be brought about through bringing the two offices under one head, the Committee strongly inclines to the view of those members who contend that it would not be in the interest of good feeling in the Society to provide a plan whereby either the Secretary of the Society is charged with the conduct of only one of the Society's journals, or the Editor of one of its journals with duties affecting all of the Society's publications.

A continuance of the present arrangement is therefore recommended. In this connection the Committee wishes to suggest that, in the interest of clarity, future statements showing the cost of conducting these offices indicate a division between the cost of handling the circulation lists, which is planily a journal expense, and that of conducting the other activities of the Secretary's office; also, that the Secretary's report be made in greater detail in order that analysis of receipts and disbursements may be more readily made; and that in published statements of membership the actual paid up membership be given as well as the total membership, which, under the Constitution, includes members in arrears for two years.

# NET RETURNS FROM ADVERTISING

Much interest has centered in the question of whether or not the Society is getting proper net re-from its advertising pages. This is a problem calling for special experience and intimate knowlturns from its advertising pages. edge of the factor.

From a source believed to be authentic, the Committee has obtained the opinion that the present arrangement under which the Society for twenty-five per cent. of gross receipts is relieved of all expense in connection with its advertising, except that of printing, is an arrangement entirely favorable to the Society, yielding larger net returns than could reasonably be expected were the Society to maintain its own advertising office. It is therefore recommended that the present arrangement be continued.

# CHEMICAL NEWS SERVICE

The suggestion coming from certain quarters, that Chemical News Service be either curtailed or discontinued, the Committee believes to be ill advised. The Committee finds that the Press of the country is making good use of our Chemical News Service, and, believing that the future of chemistry in America is in no small measure beholden to the work of properly placing our science before the public, the Committee recommends a continuance of our present program.

# NEWS EDITION OF Industrial & Engineering Chemistry

As a new medium for getting chemistry to the public, in addition to providing more matter of timely personal interest for the members, the Committee heartily endorses the News Edition of Industrial & Engineering Chemistry. Since, like the journal of which it is an off-shoot, it bids fair to become selfsupporting through the advertising it carries, there would appear to be no good argument against its continuance.

#### OUR PUBLICATIONS AS A WHOLE

The Committee believes that the importance of maintaining unimpaired the Society's present unequalled publications is too evident to need defense, as is also the importance of maintaining proper

balance in our publication program between pure science and its industrial application

The Committee is inclined to look with disfavor, therefore, upon the proposal from certain quarters to reduce the cost of membership through limiting the number of journals to be received, at least unless it can be shown that this could be done without crippling the publication of research in the pure science. The Committee is informed that it costs on the average as much to put our journals on the press preparatory to printing the first copy as it does to print and distribute the whole 14,000 odd copies now distributed, while in the case of Chemical Abstracts the first cost is much greater than that for Estimates furnished the Committee show that reduction in cost of memprinting and distributing. bership through giving a choice of journals is not feasible because of the large first cost and relatively small cost of printing extra copies.

The Committee therefore recommends that there be no change in our present publication pro-

As a detail favoring constructive journal management, the Committee favors the election of the

As a detail rayoring constructive journal management, the Committee layors the election of the Editors for three year terms following the first year of probation as now provided in the election of the Secretary and of the Treasurer.

To this end it is recommended that ARTICLE IV, Section 5 (c) of the Constitution be supplemented by the provision: "If re-elected, an Editor shall be elected by the Council to serve a term of three years, beginning with the first day of January, or until his successor shall have been duly chosen."

# MORE MONEY TO LOCAL SECTIONS

From two sources comes the request that more money be used in furthering the welfare of the Local Sections. While the Committee believes that Local Sections might profitably employ larger funds for improvment of their programs and for increasing membership in the Society, it favors at least a postponement of such increase until it can be made without the use of funds needed by the Society's publications.

## THE 1923 BUDGET

The thought apparently entertained in some quarters that the Society should be able to perform its plain duty to itself and to chemistry on a much lower budget than that arranged for the current year, cannot, in the opinion of the Committee, be entertained by anyone having a knowledge of present conditions. As for some slight reduction in our budget, the Committee is unable to find any activity the sacrifice or even curtailment of which would justify the relatively small saving thus made possible. In the opinion of the Committee, the relief some are seeking must be found through increasing

the earning power of our income producing publications, and through bringing into the Society those who, though clearly eligible for membership under any reasonable qualifications, still are not supporting the cause. Reducing the cost of membership by increasing the number of those who should thus be aiding in the advancement of chemistry in America is much more worthy of American chemists than an effort to bring about such reduction through curtailment of the present program of accomplishment. Let us advance, not retreat.

That it may be clear just where it is felt that emphasis should be placed, let it be repeated that

the Committee is unanimous and emphatic in its belief that the greates immediate need of the American Chemical Society is some effective means for insuring a better pulling together on the part of its members.

Specific recommendation to this end has been made.

Furthermore, the Committee believes that some means must be found for bringing about a beller professional spirit in the Society and a greater appreciation of the value of membership.

All to the end that the American Chemical Society may work more effectively for THE ADVANCEMENT OF CHEMISTRY AND THE PROMOTION OF CHEMICAL RESEARCH.

Respectfully submitted,

A. V. H. Mory, Chairman Geo. L. Coyle L. C. Drefahl GRAHAM EDGAR J. N. SWAN

Committee on Progress in Society Procedure

H. C. Parmelee will independently discuss the Society's publications and the intimately related subject of Finances at the New Haven Meeting.

R. E. Swain has been abroad since January and it has not been possible to secure his signature to this report. However, he has expressed himself as being in harmony with the main features, as set forth in a preliminary draft placed in his hands before he left. A. V. H. M.

A Minority Report by H. C. Parmelee, covering certain sections only of the Report of the Committee on Progress in Society Procedure, was read in full and carefully considered by the Council, and it was voted that the Secretary should file the Minority Report with thanks to H. C. Parmelee for bringing his ideas to their attention.

It was voted that the Committee be discharged with the thanks of the Council for the time, thought and care they have given to the preparation of the report.

Following the report a unanimous vote of confidence carried by a rising vote was given to H. E. Howe for his conduct of Industrial and Engineering Chemistry.

A vote of thanks was then proffered to the chairmen and members of the local committees at New Haven, to the President and corporation of Yale University, to the New Haven Chamber of Commerce, to the officials of the manufacturing plants opened to the members, and to all others to whom the Society owed thanks for the generous hospitality given us at New Haven.

On recommendation of a committee of chairmen and secretaries of Divisions, it was voted first, that the Secretary of the Society be instructed to mail the final program of meetings not less than ten days before the date of the Council meeting; second, that the final date of acceptance from authors of titles of papers be set at least one month before the date of the Council meeting; third, that the Secretary be instructed to allow at least ten days between this date and the date upon which the final program must be in his hands.

President Franklin appointed the committees for April, 1923, to April, 1924, as printed on the third page of this and subsequent issues of the Journal.

The Council then adjourned.

CHARLES L. PARSONS, Secretary

# MEMBERS ELECTED BETWEEN MARCH 15 AND APRIL 15, 1923

Abrams, Ralph B., 5 Ivy St., Boston, Mass. Ahlqvist, Harald, 17 East 42nd St., Room 1107, New York City. Ahmad, Abdel Hameed, 16 Saieda Aisha St., Khalifa Cairo, Egypt. Allan, William, Refineria El Aguila, Apartado 161, Tampico, Mexico. Altaffer, LB, 7013 Clinton Ave., Cleveland, Ohio. Anderson, Otto F., Berkshire Tioga County, N. Y. Anne, Charles Turnbull, 2020 Venango St., Philadelphia, Pa. Ashby, George E., 207 Pearl St., New York City. Barendrecht, H. P., Heerenstraat 67, Ryswyk, Holland. Bean, Harold J., Harvard Medical School, Boston, Mass. Bellows, L. A., 529 Grand Ave., Waukegan, Ili. Berry, Edward R., General Electric Co., West Lynn, Mass. Bishop, H. E., 409 Edgecombe Ave., New York City. Blocher, Edmond Le Roy, Plumville, Pa. Boyles, Alfred, P. O. Box 185, Chapel Hill, N. Car. Brand, Erwin, Montefiore Hospital, Gun Hill Road, New York City. Burke, Thomas Francis, 14 Berndt St., Pawtucket, R. I. Cady, John E., 53 Whittier Place, Indianapolis, Indiana. Carlsmith, L. E., 37 Lee St., Cambridge, Mass. Chiao, H. L., P. O. Box 104, Oxford, Ohio. Cliffe, Albert, E. W. Gillett Co., I.td., Fraser Ave., Toronto, Canada, Concannon, C. C., Chemical Division, Department of Commerce, Washington, D. C. Cunningham, Mary, 27 Clarence Terrace, Bollington, nr. Macclesfield, Cheshire, England. Demarche, Walther, 524 Rue de Herve, Bois de Breux, Liege, Belgium. Dingman, Arthur Hervey, Brunner Mond, Canada, Ltd., Amherstburg, Ont., Canada. Dresher, Austin Conrad, 227 W. Queen Lane, Germantown, Philadelphia, Pa. Dunn, Wilder, Dept. of Health, Municipal Bldg., Dallas, Texas. Eaton, Richard Victor, Lakeside, Seldown, Poole, Dorset, England. Ellis, Ridsdale, 1524 Monadnock Building, Chicago, Ill. Fackler, Louis K., 191 Sixth St., near Van Alst Ave., Long Island City, N. Y. Farrell, James L., 401 West Marvin St., Waxahachie, Texas. Fitz, Howard I., 37 Rockland St., Melrose Highlands, Mass. Fletcher, Richard Jaques, Chemical Works, North Geelong, Victoria, Australia. Flynn, Oscar R., 673 Springdale Ave., East Orange, N. J. Forni, Mario R., via Moscova 58, Milano 10, Italy. Frost, Robert B., 60 West Market St., Bethlehem, Pa. Galbraith, Freeman D., 2709 Rio Grande St., Austin, Texas. Georgi, Edmund A., Edgemont Road, Scarsdale, N. Y. Gil, Pedro, College of Agriculture, Mayaguez, Porto Rico. Gnadinger, Chas. B., 4941 Upton Ave., So., Minneapolis, Minn. Goodwin, R. C., University Station, Austin, Texas. Govea, Herminio, P. O. Box 135, College Station, Texas, Greenblatt, Jacob, 2933 Turner St., Philadelphia, Pa. Gross, A. Albert, 31 So. Hartley St., York, Pa. Gulezian, Charles E., 5636 Catharine St., Philadelphia, Pa. Harbeck, E. O., 538 Lafayette St., Grand Haven, Mich.

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Holliday, F. A., P. O. Drawer 636, Laramie, Wyoming,
Hood, G. Raymond, Dingmans Ferry, Pike County, Pa.
Hunt, Forrest G., 113 Church St., M. I. T. Club House, Winchester, Mass.
Hutchison, Robert Harris, c/o H. K. Mulford Co., 640 N. Broad St., Philadelphia, Pa.
Johnson, Frederick O., Canada Glue Co., Ltd., Brantford, Ont., Canada.
Karlberg, Robert, Holmans Bruk, Norrkoping, Sweden.
Keeler, Earl A., Brown Instrument Co., Wayne & Windrum Ave., Philadelphia, Pa.
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Lieu, Natsen, 407 E. Huron, Ann Arbor, Mich.
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Mac Tavish, D. A., Quaker Oats Co., 102 So. Howard St., Akron, Ohio.
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Rau, Kandlur Panduranga, Tata Oil Mills Co., Ltd., Tatapuram P. O. Cochin State South, India.
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Rivlin, Benjamin A., 1410 W. Woodruff Ave., Toledo, Ohio.
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Roser, Wilhelm, Farbwerke vorm, Meister Lucius & Bruning, Hoechst-on-Main, Germany.
Ruch, Elden H., 66 Russel Ave., Akron, Ohio.
Sandstedt, Rudolph M., 3119 Dudley St., Lincoln, Neb.
Schwartz, Kevie Waldemar, 21 E. 117th St., New York City.
Seavy, M. J., 153 West 23rd St., New York City.
Seko, Masatune, Tohoku Imperial University, Kogakubu Kwagakukogakkwa, Sendai, Japan.
Shah, C. C., Box 135, Mass. Inst. of Tech., Cambridge, 39, Mass.
Shaw, Hubert G., School of Technology, Atlanta, Ga.
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Smith, J. Frank, 425 No. 37th Place, Los Angeles, Cal.

Smith, Sterling B., 278 Exchange St., New Haven, Conn.

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Ullah, Mohammad Sana, Archaeological Chemist in India, Dehra Dun, India.

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van Loon, Chr., Jurgens Oliefabrieken, Zwyndrecht, Holland.

Van Orden, Paul Wm., 99 Blanch St., Houghton, Mich.

Van Wirt, A. E., 626 Stewart Ave., Ithaca, N. Y.

Von Bichowsky, Foord, 1412 San Fernando Road, Glendale, Cal.

Webster, David L., P. O. Box 52, Stanford University, Cal.

Wedgewood, Paul E., College of Medicine, Eden Ave., Cincinnati, Ohio.

Wescott, Blaine B., 1739 Lilac St., Pittsburgh, Pa.

Whitman, J. L., 15 E. Bloomington St., Iowa City, Iowa.

Winchester, Geo. W., 1343 Newport Ave., Detroit, Mich.

Winterheimer, Louis C., Silliman Institute, Dumaguete, Philippine Islands.

Woodring, Ralph W., Bethlehem City Laboratory, 3rd & Adams Sts., Bethlehem, Pa.

Yancey, William Paul, 1625 Ripley St., Davenport, Iowa.

Young, Andrew H., 401 Campbell Ave., Schenectady, N. Y.

## CORPORATION MEMBERS ELECTED

The Ault & Wiborg Co., Cincinnati, Ohio.

# MEETINGS OF THE SECTIONS

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

## AKRON SECTION

The second regular meeting of the Section was held on March 20, when D. P. Barnard of the Massachusetts Institute of Technology gave a talk on "The Automotive Fuel Situation."

W. J. Kelly, Secretary

# AMES SECTION

On February 25 and 26, the members of the Section attended two lectures, "Atomic Structure," and "The Periodicity of the Elements," respectively, by A. Somerfield, professor of mathematical physics at the University of Munich.

H. M. McLaughlin, Secretary

#### ARKANSAS SECTION

At a meeting of the members of the Section, held on February 28, H. E. Howe, editor of *Industrial and Engineering Chemistry*, spoke on "Chemistry and Business."

J. W. READ, Secretary

## CALIFORNIA SECTION

The 138th regular meeting of the Section occurred on April 6, at the Engineers' Club, San Francisco, Cal. Austin F. Rogers, of Stanford University, spoke on "The Structure of Matter as Revealed by X-Rays." E. D. Eastman, of the University of California, presented the subject in its relation to physical chemistry.

L. H. Duschak, Secretary

# CHICAGO SECTION

At the regular monthly meeting of the Section, held on March 23, F. B. Dains, of the University of Kansas, spoke on "Chemistry in Early Antiquity." Following is a list of subjects discussed in the group meetings, together with names of members who led the discussion in each group: "Some Chemical Theories," by W. R. Smith, of Lewis Institute; "A Few Early Methods of 'Packing-House' Chemistry," by Paul Rudnick, of Armour & Company; "The Chemist in State Control of Manufactured Foodstuffs," by T. J. Bryan, of the Calumet Baking Powder Company; "Some Chemical Reminiscences," by W. A. Converse, of the Dearborn Drug & Chemical Company; and "Chemistry for the Railroad," by G. M. Davidson, of the Chicago & Northwestern Railway.

On April 20, Ellwood Hendricks spoke before the meeting of the Section, taking as his subject "Obligations in Chemistry." The usual group meetings were held after the address of the evening.

S. L. Redman, Secretary

#### CINCINNATI SECTION

The 258th regular meeting of the Section was held on April 11, when Lauder W. Jones, of Princeton University, addressed the members, taking as his subject "Nitrogen, A Theme with Variations."

On April 23, Ellwood Hendricks addressed the meeting of the Section. His subject was "Obligations in Chemistry."

A. O. SNODDY, Secretary

#### CLEVELAND SECTION

On March 20, Edwin E. Slosson, of Washington, D. C., lectured before the meeting of the Section, his subject being "Chemistry Applied to Industry."

The local Section, in cooperation with the Cleveland Engineering Society, held a special meeting on Tuesday, April 3, when H. A. Gardner, of the Institute for Paint and Varnish Research, Washington, D. C., gave an illustrated lecture on "Research in the Paint and Varnish Industry."

At the regular meeting of the Section, held on April 23, E. C. Franklin, president of the American Chemical Society, addressed the members, his subject being "The Ammonia System of Compounds."

H. S. Booth, Secretary

## CONNECTICUT VALLEY SECTION

The Section held a joint meeting with various technical societies on April 21. After an inspection trip through the new plant of the Hartford Rubber Works, the meeting was addressed by B. J. Lemon, of that company, on the subject, "Tire Factors that Measure Vehicle Costs."

PAUL SEREX, JR., Secretary

## CORNELL SECTION

On April 18, E. C. Franklin, president of the American Chemical Society, addressed the department of chemistry of Cornell University and the members of the Section. His subject was "The Ammonia System of Compounds."

F. E. HANCE, Secretary

## DELAWARE SECTION

On April 18, H. W. Jordan, of Syracuse, N. Y., addressed the members of the Section, taking as his subject, "The Chemist as a Citizen. A Forecast of the Trend of the Times."

J. W. STILLMAN, Secretary

## DETROIT SECTION

At a joint meeting of the Associated Technical Societies of Detroit, of which the local Section is a member, held on March 19, Walter Rosenhain, director of the metallurgical department of the National Physical Laboratory of England, gave an address on the subject, "Strain and Fracture in Metals."

S. R. Wilson, Secretary

## EASTERN NEW YORK SECTION

At the regular meeting of the Section which occurred on March 23, Leon W. Parsons, of the Tide Water Oil Co., spoke on "Some Applications of Colloids to the Petroleum Industry."

At the regular monthly meeting of the Section, held on April 20, Zay Jefferies spoke on "Hardness of Metals."

E. H. Darby, Secretary

#### INDIANA SECTION

The following subjects were presented at noonday luncheons of the Section held on Tuesday of each week at Indianapolis: March 13, "The Manufacture of Beet Sugar," by Wallace Benson; March 20, "The Electronic Vibrations of Abrams," by Otto H. Gripe. At the regular meeting of the Section, held on April 13, G. H. A. Clowes, of Eli Lilly & Company, Indianapolis, Ind., spoke on the subject of "The Development of Iletin as Used in the Treatment of Diabetes." On April 21, the members of the Section were invited to Lafayette, Ind., as guests of the Purdue Section, at which time, H. C. Parmelee, editor of Chemical and Metallurgical Engineering, was the speaker.

WILLIAM HIGBURG, Secretary

#### IOWA SECTION

At a meeting of the Section, held on March 28, J. A. Hynes, of Chicago, spoke on the subject, "The Chemist in the Customs Service."

G. H. COLEMAN, Secretary

## LEHIGH VALLEY SECTION

On April 14, E. C. Franklin, president of the American Chemical Society, addressed the members of the Section, his subject being "The Ammonia System of Compounds."

R. H. BOGUE, Secretary

#### LOUISIANA SECTION

The Section, on March 21, had as its speaker, E. C. Franklin, president of the American Chemical Society, who spoke on "The Ammonia System of Compounds."

H. R. STEVENS, Secretary

#### MARYLAND SECTION

On March 29, E. C. Franklin, president of the American Chemical Society, addressed the members at the 64th meeting of the Section. Dr. Franklin's subject was "The Ammonia System of Compounds."

At the 65th regular meeting of the Section, held on April 27, W. O. Mitscherling spoke on "Cellulose Silk."

Adolph Harvitt, Secretary

# MICHIGAN AGRICULTURAL COLLEGE SECTION

At a banquet and open meeting given by the Section on March 15, J. E. Harris, of the Western Electric Co., New York City, spoke on the subject of "Putting Electrons to Work."

EDWARD ELDRIDGE, Secretary

## MILWAUKEE SECTION

At the regular monthly meeting of the Section, held on March 23, Harold C. Bradley of the University of Wisconsin addressed the Section on the subject "The Chemical Mechanism of Atrophy in the Animal Body."

ALFRED A. CHAMBERS, Secretary

## MINNESOTA SECTION

On February 19, the Minnesota Section received an invitation from the N. W. Chapter of the American Society for Steel Treating, to hold a joint dinner, followed by a lecture by Paul D. Merica, of the International Nickel Company, his subject being "Nickel and Nickel Alloys."

On April 17, Lauder W. Jones, of Princeton University, addressed the meeting of the Section. His subject was "Radicalism in Chemistry."

L. M. HENDERSON, Secretary

## NASHVILLE SECTION

The local Section had as its speaker, on March 22, E. C. Franklin, president of the American Chemical Society, who spoke on "The Ammonia System of Compounds."

H. A. WEBB, Secretary

#### NEBRASKA SECTION

The 108th meeting of the Section occurred on March 13, when S. Morgulis, of the University of Nebraska, spoke on "The Chemical Transformations in the Organism."

S. B. ARENSON, Secretary

# NEW HAVEN SECTION

The regular monthly meeting of the Section was held at Bridgeport, Conn., on March 27. The speaker of the evening was R. J. McKay, of the International Nickel Company, whose subject was "Nickel and Its Alloys."

BLAIR SAXTON, Secretary

#### NEW YORK SECTION

At a special meeting of the Section, held at Rumford Hall, Chemists' Club, on April 11, had as its speaker E. C. Franklin, president of the American Chemical Society, his subject being "The Ammonia System of Compounds."

Benjamin T. Brooks, Secretary

#### NORTHEASTERN SECTION

The 184th meeting of the Section occurred on April 9. On this occasion, E. C. Franklin, president of the American Chemical Society, spoke on "The Ammonia System of Compounds."

E. B. Millard, Secretary

#### NORTHERN INDIANA SECTION

A regular meeting of the Section was held on March 21, when A. H. Sabin, of the National Lead Company, spoke on "Nature and Use of Paint Materials." George W. Blair, of the Mishawaka Woolen Company, discussed the "Laboratory from the Engineer's Standpoint."

On April 11, the Section held a joint meeting of the local chapter of the American Society for Steel Treating. H. M. Boylston, of the Case School of Applied Science, spoke on "Metallography." J. A. White, of the Clark Equipment Company, discussed the "Electric Furnace in the Foundry."

V. C. BIDLACK, Secretary

## NORTHERN WEST VIRGINIA SECTION

At a meeting of the Section, held on February 28, Lilly Bell Sefton Deatrick spoke to the members, taking as her subject "Analysis of Micro Amounts of Impurities in Battery Acids."

E. P. DEATRICK, Secretary

## OREGON SECTION

The 52nd meeting of the Section, held on March 31, was given over to the discussion of the subject, "New Methods of Estimating Hemoglobin, Sugar and Uric Acid in the Blood," lead by H. D. Hasins, E. E. Osgood, W. O. Holbrook and Thomas Watson.

F. L. SHINN, Secretary

# PHILADELPHIA SECTION

On April 12, E. C. Franklin, president of the American Chemical Society, addressed the meeting of the Section. His subject was "The Ammonia System of Compounds."

I. HOWARD GRAHAM, Secretary

## PITTSBURGH SECTION

The 186th regular meeting of the Section occurred on March 26, when E. C. Franklin, president of the American Chemical Society, addressed the members. His address was on "The Ammonia System of Compounds."

The 187th regular meeting was held on April 12. Prof. Giuseppe Bruni, director of research department, Pirelli & C., Milan, Italy, spoke on "Italy's Part in Chemical Scientific Development."

E S. STATELER, Secretary

#### PUGET SOUND SECTION

At a joint meeting of the Section with the Olympic Chemical Club of Tacoma, Wash., held on March 24, the members were addressed by James Kendall, of Columbia University, New York City. His subject was "Isotopes." R. W. Ellison, Secretary

#### PURDUE SECTION

The Section held a joint meeting with the Indiana Branch of the American Pharmaceutical Association on March 24. Two lectures, as follows, were given: "Use of Solutions of Inorganic Salts as Permanent Color Standards," by M. G. Mellon; and "Prosecutions Under the Shirley Amendment of the Pure Food and Drug Act," by R. E. Doolittle.

MARGUERITE G. MALLON, Secretary

## RHODE ISLAND SECTION

On April 10, E. C. Franklin, president of the American Chemical Society, addressed the members of the Section. His subject was "The Ammonia System of Compounds."

NELSON BARLOW, Secretary

#### ROCHESTER SECTION

The 151st meeting of the Section occurred on March 5, when Marston T. Bogert, of Columbia University, spoke on "Perfumes, Natural and Synthetic."

The 153rd meeting was held on March 26. At that time, Hugh S. Taylor, of Princeton University, addressed the members, his subject being "Some Problems of Catalysis."

The 154th regular meeting of the Section was addressed by E. C. Franklin, president of the American Chemical Society, on the subject, "The Ammonia System of Compounds."

ERLE M. BILLINGS, Secretary

## SACRAMENTO SECTION

At the regular meeting of the Section, on January 13, the following officers for 1923 were elected: G. H. P. Lichthardt, chairman; C. F. Hoyt, vice chairman; George E. Colby, councilor; and J. H. Norton, secretary-treasurer.

The sixth regular meeting of the Section occurred on March 17. After a short business meeting, the members enjoyed a personally conducted excursion through the Southern Pacific Railway shops, mills, laboratory, and electric steel foundry.

J. H. NORTON, Secretary

#### SAINT LOUIS SECTION

At a special meeting of the Section, on March 24, E. C. Franklin, president of the American Chemical Society, gave his lecture, entitled "The Ammonia System of Compounds."

The regular monthly meeting of the Section, held on April 12, was addressed by Lauder W. Jones, of Princeton University, who took as his subject, "Fulminates and Bi-valent Carbon."

H. A. Carlton, Secretary

#### SAVANNAH SECTION

The regular monthly meeting of the Section was held on March 8. C. B. Hicks, of Parke, Davis & Company, gave a talk on "The Standardization of Drugs."

On April 12, Herbert S. Bailey addressed the members of the Section, his subject being "Paints and Paint Pigments."

HERBERT P. STRACK, Secretary

## SOUTHEAST TEXAS SECTION

At the 21st regular meeting of the Section, held on March 7, E. C. Franklin, spoke to the members on "The Ammonia System of Compounds." P. S. Trison, Secretary

## SOUTHERN CALIFORNIA SECTION

The regular monthly meeting of the Section occurred on April 20, when Charles Galton Darwin, of the California Institute of Technology, spoke on "The Periodic System."

MARK WALKER, Secretary

## SYRACUSE SECTION

On March 23, A. W. Browne, of Cornell University, addressed the members of the Section. His subject was "Azido-Dithiocarbonate, or a Reciprocal Catalytic Pair."

On April 17, E. C. Franklin, president of the American Chemical Society, spoke to the members, his subject being "The Ammonia System of Compounds."

W. P. Hicks, Secretary

## TOLEDO SECTION

At the regular meeting of the Section, on April 17, R. J. Cowan, of the National Malleable Castings Company, spoke on "Hardness and Plastic Deformation of Metals."

GUY E. VAN SICKLE, Secretary

#### UNIVERSITY OF ILLINOIS SECTION

A series of three lectures, by Walter Rosenhain, of the British National Physical Laboratory, England, were delivered at the University of Illinois. On March 20, his first lecture, under the auspices of the local Section, was given. 'The subject was "Metallurgical Research at the National Physical Laboratory, Teddington, England." On March 21, his lecture was on "The Structure and Constitution of Alloys;" and on March 22, he spoke on "Strain, Its Relation to and Fracture of Metals."

On March 24, F. B. Dains, of the University of Kansas, spoke before the members of the Section, his subject being "Chemistry in Early Antiquity."

At a joint meeting of the local Section and the Phi Lambda Upsilon, on Friday, April 13, Lauder W. Jones, of Princeton University, spoke on "Radicalism in Chemistry."

D. T. Englis, Secretary

## VIRGINIA SECTION

The 57th meeting of the Section was held on April 13, when Graham Edgar, of the University of Virginia, gave an address on "Atomic Weights, Isotopes and the Breaking Up of Atoms."

W. G. CROCKETT, Secretary

## WASHINGTON, D. C. SECTION

The 340th regular meeting of the Section occurred on March 28, at which time E. C. Franklin, president of the American Chemical Society, spoke on "The Ammonia System of Compounds."

The 341st regular meeting, held on April 12, had as its speaker, Carl L. Alsberg of the Food Research Institute, Stanford University, Calif., whose subject was "Agricultural and Fuel Supply as the Limiting Factors in the Food Supply of the World."

The Section held a joint meeting with the Washington Academy of Sciences and the Philosophical Society of Washington on April 17. The speakers of the evening were F. G. Donnan, professor of chemistry, University College, London, England, and James C. Irvine, principal and vice-chancellor, University of St. Andrews, Scotland, their subjects being "Membrane Equilibria," and "Composition of Starches," respectively.

J. B. Reed, Secretary

#### DECEASED

## Proceedings

## COUNCIL

MEMBERS ELECTED BETWEEN APRIL 15 AND MAY 15, 1923

Alvaro, Albert, 466 Rua Barata Ribeiro, Rio de Janeiro, Brazil.

Barnes, Garrett H., Jr., Y. M. C. A., 259 South Main St., Akron, Ohio.

Bell, J. D., Franklin, La.

Bemisderfer, Franklin Ray, 2075 E. 83rd St., Cleveland, Ohio.

Binnall, F. C., 811 Broad St., Chattanooga, Tenn.

Bowman, John R., 155 N. Dithridge St., Pittsburgh, Pa.

Briggs, Richard M., 26 Albemarle St., Rochester, N. Y.

Butts, Durain C., 60 E. Lane Ave., Columbus, Ohio.

Charpentier, E. R. H., Laboratory of Pure Science, Nela Park, Cleveland, Ohio.

Chow, H. S., 159 Austin St., Cambridge, Mass.

Colbert, James C., 419 N. Dubuque St., Iowa City, Iowa.

Cooley, Warren K., 91 Lenox Ave., Providence, R. I.

Corran, John William, 86 Upper Hill St., Princes Park, Liverpool, England.

Coughlan, W. D., 1415 Para St., Alameda, Cal.

Crabb, John Power, 27 Maryland St., Dorchester, Mass.

de Graaff, Antonius de, Library Department, Philips Glowlampworks, Eindhoven, Holland.

De Holczer, Lewis, 4101 Wellington Ave., Chicago, Ill.

Dixon, Herbert C., 800 Highland Ave., Johnstown, Pa.

Elder, Harry L., Grove City College, Grove City, Pa.

Finch, Myron W., 31 Lincoln Blvd., Kenmore, N. Y.

Follwell, Edward Harris, Box 33, Delaware, Ohio.

Foster, Sydney P., 1515 W. Monroe St., Chicago, Ill.

Freedman, L. H., 686 Washington St., Brookline, Mass.

Gaskill, E. C., 532 Columbia Ave., Palmerton, Pa.

Gilson, Richard W., 3824 S. Wisconsin St., Los Angeles, Cal.

Gordon, Samuel M., 123 Quadrangle, Iowa City, Iowa.

Hall, J. Alfred, Exchange Research Lab., San Dimas, Cal.

Harden, Wilton Cope, 9 Melvin Ave., Catonsville, Md.

* Healy, Rufus A., Harkness & Cowing Co., St. Bernard, Cincinnati, Ohio.

Hesselink, W. F., Nieuwe Kade 4, Arnhem, Netherlands.

Hirsch, Henry D., 1706 E. 56th St., Chicago, Ill.

Hoyt, Jonathan, Stauffer Chemical Co., Stege, Cal.

Isermann, Max, 4-6 Platt St., New York City.

Jasper, Joseph J., 240 Eastern Ave., S. E., Grand Rapids, Mich.

Jones, Minor C. K., Spring Gardens Plant, Con. Gas Elec. Light and Power Co., Baltimore, Md.

Kastler, Arthur O., 3125 Chestnut St., New Orleans, La.

Keans, Lee A., O'Bannon Co., West Barrington, R. I.

Ketchum, Pierce, 407 West California St., Urbana, Ill.

Kidd, William A., Hag Abdalla, Sudan, Africa.

Kunerow, Reinhold, Consumers Compressed Yeast Co., Oakland, Cal.

Leahy, James F., Hayes St., Natick, Mass.

Lehew, Donald M., 190 West 9th Ave., Columbus, Ohio.

Link, Karl Paul, Room 401, 145 Iota Court, Madison, Wis.

Mann, Matthew D., Jr., 625 Locust St., Roselle, N. J.

McComas, James A., Con. Gas. Elec. Light & Power Co., Spring Gardens Station, Baltimore, Md.

McGar, Benjamin H., Chase Metal Works, Waterbury, Conn.

McGill, Martin V., 1444 East Erie Ave., Lorain, Ohio.

Miller, Palmer, 106 S. Lake Ave., Pasadena, Cal.

Minor, Henry R., 542 Fifth Ave., New York City.

Montgomery, Wallace, 2814 Broadway St., New Orleans, La.

Parker, Henry Cole, Kent Chemical Laboratory, University of Chicago, Chicago, Ill.

Parsons, Llewellyn B., 309 E. Gorham St., Madison, Wis.

Perry, Gerald E., 145 Henry St., Brooklyn, N. Y.

Pike, Frederick A., 2351 N. Woodstock St., Philadelphia, Pa.

Powell, C. W., Jr., 445 Reber Ave., Waterloo, Iowa.

Raudenbush, Earl, Box 4188, Miami, Florida. Rice, Ambrose Clark, Grand Island College, Grand Island, Neb. Robson, Homer Louis, Dept. of Chem., Univ. of Sask., Saskatoon, Sask., Canada. Rogers, Maurice, Roxbury School, Cheshire, Conn. Ronzoni, Ethel, 6952 Clayton Road, St. Louis, Mo. Schell, Charles F., 48 Ash St., Braintree 84, Mass. Schwert, Wm. Harold, 10622 Helena Ave., Cleveland, Ohio. Sjollema, B., Biltstraat 122, Utrecht, Holland. Snyder, Carl F., Bureau of Standards, Washington, D. C. Sonnenblick, Ira, 588 Herkimer St., Brooklyn, N. Y. Stacy, Lucius E., 332 E. St., North Wilkesboro, N. Car. Stambaugh, Philip S., 117 Woodbine, Youngstown, Ohio. Stenbuck, Frederick A., New York University, New York City. Stern, Sidney M., 506 West 136th St., New York City. Story, R. G., 1440 Mulberry St., Lincoln, Neb. Stubbs, Fred G., 1346 N. H. St., Lawrence, Kans. Tharaldsen, F., Josefinegate 18, Kristiania, Norway. van der Hoeven, B. J. C., 55 Hanson Place, Brooklyn, N. Y. Van Vleet, Harley Samuel, 1308 E. Ann St., Ann Arbor, Mich. Verkade, G. E., Heimraadssingel 44, Rotterdam, Holland. Vetter, Joseph J., Howland Ave., Route No. 2, Hackensack, N. J. Wallage, Stanley T., 1429 18th St., Denver, Col. Watkins, Willard Merrill, 4805 Eastern Ave., Cincinnati, Ohio. Werkenthin, Theodore Albert, 4312 Caswell Ave., Austin, Texas. Wharton, William B., 201 Keystone Building, Pittsburgh, Pa. White, Joseph Dixon, Guilford College, N. Car. Williams, Glenn A., 573 Elms St., Akron, Ohio. Yoshioka, Susumu, Miike-Senryo-Kogyosho, Omuta Fukuokaken, Japan.

### CORPORATION MEMBER

Federal Color Laboratories, Inc., Norwood, Ohio.

## MEETINGS OF THE SECTIONS

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St. N. W., Washington, D. C.)

## CHICAGO SECTION

The annual Willard Gibbs dinner and award of medal for 1923 was held on May 25, at the City Club, Chicago, Ill. The reception and dinner was followed by the presentation of the medal by its founder, William A. Converse, and an address by the medallist, Professor Julius Stieglitz, chairman of the department of chemistry, University of Chicago, whose subject was "The Theory of Color Production in Dyes."

LEE F. SUPPLE, Secretary

## CINCINNATI SECTION

The 259th regular meeting of the Section occurred on May 16, when E. Emmet Reid, head of the department of chemistry in Johns Hopkins University, spoke on "The Influence of Sulfur on the Color of Dyes."

A. O. Snoddy, Secretary

## COLORADO SECTION

On April 25, F. C. Gilbert, of the American Smelting and Refining Co., addressed the meeting of the Section.

RUTH B. VERTREES, Secretary

## CONNECTICUT VALLEY SECTION

The regular monthly meeting of the Section was held at Middletown, Conn., May 5. A business meeting was held in the afternoon, and in the evening there was an address by W. H. Whitcomb, of the United States Rubber Co., New Haven, Conn., his

subject being "Some Applications of Chemistry to the Compounding and Vulcanization of Rubber Goods."

Paul Serex, Jr., Secretary

### CORNELL SECTION

On April 30, the following papers were presented before the meeting of the Section: "Germanium from American Zinc Blendes," by E. B. Johnson; and "The Effects of Certain Pigments on the Rate of Oxidation from Linseed Oil," by A. E. Van Wirt.

At the regular monthly meeting, held on May 14, the following program was presented: "A New Halogenoid Hydracid and Some of its Derivatives," by G. B. L. Smith; and "Vapor Pressure of Gasolines," by E. B. McConnell. F. E. Hance, Secretary

#### DELAWARE SECTION

The regular meeting of the Section occurred on May 16, when H. E. Howe, editor of Industrial and Engineering Chemistry, spoke before the members on the subject, "Some Problems of Scientific Publication."

J. W. STILLMAN, Secretary

## DETROIT SECTION

Dr. Edward C. Franklin, president of the American Chemical Society, addressed the meeting of the Section, held on April 25, his subject being "The Ammonia System of Compounds."

S. R. Wilson, Secretary

#### HAWAIIAN SECTION

On April 20, Miss C. C. Miller, of the University of Hawaii, address the meeting of the Section, her subject being "Vitamins."

RONALD Q. SMITH, Secretary

## INDIANA SECTION

On May 3, Edward C. Franklin, president of the American Chemical Society, delivered his lecture, "The Ammonia System of Compounds," before the regular meeting of the Section.

On May 11, the following programs was presented by the Section: "The Manufacture of Glue," by S. N. Wentworth, of the American Glue Company; "Garbage Disposal," by E. W. McCullough, engineer for the Garbage Disposal Plant, City Sanitary Commission; and a discussion of these subjects was lead by Paul Smith of Indianapolis.

William Higburg, Secretary

## IOWA SECTION

The regular monthly meeting of the Section occurred on April 27 and 28, in connection with the Iowa Academy of Science.

A meeting of the Section was also held on May 11, when E. C. Franklin, president of the American Chemical Society, spoke on "The Ammonia System of Compounds."

G. H. COLEMAN, Secretary

## KANSAS CITY SECTION

The 165th meeting of the Section was held on April 28. H. E. Hancock, chemist of the Sewall Paint and Glass Co., gave an address on "New Ideas in the Manufacture of Paints and Varnishes."

On May 16, Lee E. Clark addressed the members on the subject, "Selling Yourself as a Chemist."

Left E. Clark, Secretary

## LEHIGH VALLEY SECTION

At a joint meeting of the Section and the Gayley Chemical Society of Lafayette College, Easton, Pa., held on May 11, Hugh S. Taylor, of Princeton University, gave an address on "Catalysis: Positive and Negative." R. H. Boour, Secretary

## LEXINGTON SECTION

The 87th meeting of the Section occurred on April 25, when a visit was made to the Lexington Sewage Disposal Plant and the phosphate mine at Midway, Ky.

The 88th meeting was held on May 17, when E. Emmet Reid of Johns Hopkins University, addressed the Section on "The Influence of Sulfur on the Color of Dyes."

E. L. JACKSON, Secretary

## MAINE SECTION

On May 11, F. F. Oplinger, of the University of Maine, addressed the members, his subject being "Application of the Electron Theory of Valence to Organic Chemistry."

N. E. WOLDMAN, Secretary

#### MICHIGAN AGRICULTURAL COLLEGE SECTION

At the meeting of the Section, held on April 18, Ellwood Hendrick, of New York City, spoke on "The Sense of Smell."

On April 30, E. C. Franklin, president of the American Chemical Society, addressed the members, his subject being "The Ammonia System of Compounds."

The following officers for 1923 have been elected: C. S. Robinson, chairman; Ward Giltner, vice chairman; C. D. Ball, secretary; O. B. Winter, treasurer; and D. T. Ewing, councilor.

E. F. ELDRIDGE, Secretary

#### MILWAUKEE SECTION

The regular meeting of the Section was held on April 19, when Lauder W. Jones, of Princeton University, addressed the members on the subject, "Nitrogen: A Theme with Variations."

On May 8, E. C. Franklin, president of the American Chemical Society, gave his lecture on "The Ammonia System of Compounds."

ALFRED A. CHAMBERS, Secretary

## MINNESOTA SECTION

At the meeting of the Section, held on May 16, E. C. Franklin, president of the American Chemical Society, lectured on "The Ammonia System of Compounds."

L. M. HENDERSON, Secretary

## NASHVILLE SECTION

The following papers were presented at the meeting of the Section, held on April 27: "Problems in the Manufacture of Sweet Potato Products," by J. E. Copenhaver, of the department of chemistry, Vanderbilt University; and "Progress of a Study of the Preparation of an Organic Compound by Electricity," by B. F. Armendt, of Vanderbilt University.

H. A. Webb, Secretary

## NEBRASKA SECTION

The 109th regular meeting of the Section, held on April 12, was addressed by H. P. Cady, of the department of chemistry, University of Nebraska, his subject being Radium and Radioactivity."

S. B. Arenson, Secretary

## NORTH CAROLINA SECTION

The spring meeting of the Section was held at The North Carolina College for Women, Greensboro, N. C., on May 5. The following program was presented: "Chemical Industries in North Carolina," by F. C. Vilbrandt; "The Chlorination of Juglone in hot Acetic Acid," by A. S. Wheeler and J. L. McEwen; "The Bromination of 2-Amino-p-xylene," by A. S. Wheeler and E. W. Constable; "The Schohl and Pedley Method for Determination of Calcium Compared with McCrudden's Volumetric Method," by J. O. Halverson and L. M. Dixon; "A New Ketone Reagent: p-Bromo-

phenylsemicarbazide by A. S. Wheeler and J. A. Bender; "The Constitution of the Dichlorohydroxyethylidene-bis-nitroanilines," by A. S. Wheeler and S. C. Smith; "Problems of the Chemist in the Textile Industry," by K. W. Franke; "A Vacuum Gage," by M. L. Hamlin; "A Peculiar Reaction Between Dichloroacetic Acid and Aromatic Amines," by A. S. Wheeler and S. C. Smith; "A Peculiar Phenomenon of the Bunsen Burner," by H. B. Arbuckle; "A Suggestion in Regard to Some Problems Relating to the Hydration of Ions," by E. E. Randolph.

The following offices were elected for 1923: J. O. Halverson, president; F. C. Vilbrandt, vice president; Paul W. Gross, councilor; and Leland B. Rhodes, secretary-treasurer.

Leland B. Rhodes, Secretary

#### NORTHEASTERN SECTION

The 185th meeting of the Section was held on May 11, in Boston, Mass. The following addresses were given: "The Chemical and Physical Aids to Diagnosis," by Allan Winter Rowe; and "Some Chemistry of the Insect World," by Gorham W. Harris.

E. B. MILLARD, Secretary

## OMAHA SECTION

The regular monthly meeting of the Section was held on May 1, at the plant of the American Smelting and Refining Co., with the following program: "The Omaha Plant, American Smelting and Refining Co., as an Industry," by A. E. Hall; "Chemistry as Applied to Lead Bullion Refining," by B. N. Kilbourn; "Chemistry as Applied to the Smelting of Non-ferrous Metals," by V. T. Price; "The Chemistry and Uses of Bismuth," by J. O. Betterton; and "The Laboratory and Assaying Department, Its Purpose and Relation to the Plant," by E. Wurgler.

R. N. Perkins, Secretary

## PHILADELPHIA SECTION

At the meeting of the Section, held on May 17, Edgar Fahs Smith gave a short talk on M. Carey Lea, a former prominent chemist of Philadelphia, born one hundred years ago. There was also an address by Henry Green, of the New Jersey Zinc Co., on "Structure."

J. Howard Graham, Secretary

## PITTSBURGH SECTION

At the regular monthly meeting of the Section, held on May 17, Jacob Rosenbloom, of Pittsburgh, addressed the members on the subject "The Urologist or Water Caster in Art."

E. S. STATELER, Secretary

#### PURDUE SECTION

On April 21, Ellwood Hendrick, of New York City, addressed the meeting of the Section, his subject being "The Sense of Smell."

At the meeting of the Section, on May 2, E. C. Franklin, president of the American Chemical Society, delivered his lecture on "The Ammonia System of Compounds."

The following officers have been elected by the Section for 1923: C. B. Jordan, chairman; R. E. Nelson, vice chairman; E. G. Mahin, councilor; and M. G. Mallon, secretary-treasurer.

MARGUERITE G. MALLON, Secretary

#### ROCHESTER SECTION

The 155th regular meeting of the Section occurred on May 7, when Lincoln Burrows, of the Eastman Kodak Co., gave a lecture on "Soap and Glycerine."

On May 15, the members of the Section were invited to hear a lecture by Paul D. Foote, of the United States Bureau of Standards, his subject being "The Alchemist."

The following officers for 1923 have been elected: Edward B. Leary, chairman; Lincoln Burrows, vice chairman; Erle M. Billings, secretary-treasurer; O. I. Chormann, William Webb and Charles Hutchison, executive committee.

E. M. BILLINGS, Secretary

## SAINT LOUIS SECTION

On May 7, John R. Eoff, Jr., of Garrett & Company, St. Louis, addressed the meeting of the Section. His subject was "Some Modern Conceptions of Alcoholic Fermentation."

The Section held a joint meeting with the American Society of Mechanical Engineers and American Ceramic Society on May 18. W. B. Chapman, of Chapman Engineering Co., New York City, spoke on "Fuel Saving in Modern Gas Producers and Industrial Furnaces," and Paul V. Bunn, general secretary of the St. Louis Chamber of Commerce, gave an illustrated talk on "A Trip to Cuba, Panama and Costa Rica."

H. A. CARLTON, Secretary

## SACRAMENTO SECTION

A business meeting of the Section was held on May 9. Reports of various committees were received, future programs were discussed, and important announcements were made.

J. H. Norton, Secretary

## SOUTH JERSEY SECTION

The 20th regular meeting of the Section was held on April 26, when Winfield Scott spoke on "The Acceleration of Vulcanization in Rubber," giving a history of the discovery and use of accelerators.

W. F. Twombly, Secretary

#### SYRACUSE SECTION

On April 27, the Section elected the following officers for 1923: Ross A. Baker, president; W. B. Hicks, vice president; John H. Nair, secretary; Paul S. Craig, treasurer; A. W. Kimman, councilor.

On May 7, A. F. Holleman, of Amsterdam, Netherlands, addressed the members of the Section, his subject being "Research at the University of Amsterdam."

JOHN H. NAIR, Secretary

### TOLEDO SECTION

At the regular meeting of the Section, held on May 15, O. F. Hedenburg, of the Mellon Institute, Pittsburgh, Pa., gave an address on "Chemistry as Applied to the Insecticide Industry."

Guy E. Van Sickle, Secretary

## UNIVERSITY OF ILLINOIS SECTION

An intersectional meeting of the American Chemical Society was held with the University of Illinois Section, at Urbana, Illinois, on May 4 and 5. The following program was presented:

FRIDAY, MAY 4th-2:00 P.M.

## GENERAL MEETING

Introductory-Professor W. A. Noyes.

Address: The Ammonia System of Compounds-President E. C. Franklin.

Address: The Development of our Organic Chemical Industry-Dr. L. F. Nickell.

4:00 P.M.—Athletic Games, Urbana Country Club.

6:15 p.m.-Luncheon and Social Hour.

8:30 P.M.—Short Talk, President Franklin.

Entertainment by Alpha Chi Sigma, Iota Sigma Pi and Gamma Pi Upsilon.

## SATURDAY, MAY 5th-8:00 A.M.

## GENERAL MEETING

Popular Lecture: Home Remedies—Their Claims Versus Composition—Dr. P. N. Leach.

9:30 A.M.—GROUP MEETINGS

12:00 M.-Luncheon under auspices of Chemistry Club at the "Green Tea Pot."

2:00 P.M.—Inspection of University Buildings and Grounds.

Cars will leave from the drive in front of the Chemistry Building.

## PHYSICAL AND INORGANIC GROUP

Some Reactions in the Corona Discharge and the Temperature Corresponding to Equilibrium—Gerald L. Wendt, Standard Oil Company.

Electrolytic Polarization-H. P. Cady, University of Kansas.

The Separation of the Isotopes of Chlorine, Mercury, Cadmium and Zine—W. D. Harkins, University of Chicago.

Alpha Ray Tracks in Gases—R. W. Ryan and W. D. Harkins, University of Chicago. The Accurate Measurements of the Heats of Vaporization of Liquids—J. H. Mathews, University of Wisconsin.

The Solubility of Barium Manganate and the Equilibrium Between Manganate and Permanganate—H. I. Schlesinger, University of Chicago.

Colloidal Ferric Hydroxide and Ferric Hydroxide Gel—R. E. Wilson, Standard Oil Company.

Heats of Vaporization of Metals—M. F. Fogler and W. H. Rodebush, University of Illinois.

Total and Partial Pressures of Aqueous Ammonia Solutions—T. A. Wilson and Gerhard Dietrichson, University of Illinois.

## INDUSTRIAL GROUP

## W. J. Hoskins, Presiding

Combustion of Hydrogen and Carbon Monoxide by Various Oxides—M. J. Bradley, University of Illinois.

An Improved Apparatus for Fuel Gas Analysis—F. E. Vandeveer, University of Illinois. Report of Investigation Work in Progress by the Ceramic Department; University of Illinois—C. W. Parmelee, University of Illinois.

Muriatic Tank Cars-L. F. Nickell, Monsanto Chemical Works.

The Tantalum Electrolytic Valve—E. W. Engle, Fansteel Products Company.

The Manufacturing Laboratory of the Public Health Institute—F. C. Whitmore, Northwestern University.

Laboratory Type of High Temperature Furnace for Investigation Work on Alloys—M. M. Austin, University of Illinois.

Development of Redmanol-Frank P. Brock, Redmanol Chemical Products Company.

## ORGANIC GROUP

Some Recent Studies Concerning Organo-Magnesium Halides—Henry Gilman, Iowa State College.

The Migration of Acyl from Nitrogen to Oxygen—L. Charles Raiford, State University of Iowa.

Reminiscences in the Manufacture of Phenol Plastics—Frank P. Brock, Redmanol Chemical Products Company.

Insulin-David Klein, Wilson Laboratory, Chicago, Ill.

Recent Developments in the Manufacture and Use of Furfural—Carl S. Miner, John P. Tricky and Harold J. Brownlee, Miner Laboratories, Chicago, Ill.

## EDUCATIONAL GROUP

J. H. Walton, University of Wisconsin, Presiding.

A Quantitative Analysis of Present Aims in Teaching Freshmen Chemistry—Jacob Cornog, University of Iowa.

Outline of the Essential Topics in a College Course of Elementary Chemistry—Louis A. Test, Purdue University.

The Aims and Methods of First Year College Chemistry—James H. Ransom, James Millikin University.

D. T. Englis, Secretary

## UNIVERSITY OF MICHIGAN SECTION

On April 26, E. C. Franklin, president of the American Chemical Society, addressed the members, his subject being "The Ammonia System of Compounds."

C. C. MELOCHE, Secretary

#### VIRGINIA SECTION

The 58th meeting of the Section occurred on May 11, when R. E. Loving, of the University of Richmond, addressed the members on "The Physics of the Air."

The following officers for 1923 were elected at this meeting: Wortley F. Rudd, chairman; Hall Canter, vice chairman; L. C. Bird, secretary-treasurer; Garnett Ryland and Graham Edgar, councilors.

W. G. CROCKETT, Secretary

## WASHINGTON, D. C. SECTION

The 344th meeting of the Section occurred on May 10. The Program consisted of contributions by a considerable number of members who described novel methods for analytical work, for physical measurements, or Laboratory manipulation. In a number of cases demonstrations of unusual and new forms of apparatus were made.

J. B. REED, Secretary

#### WESTERN NEW YORK SECTION

On April 21, E. C. Franklin, president of the American Chemical Society, delivered his lecture entitled "The Ammonia System of Compounds," before the members of the Section.

R. W. Hess. Secretary

## WISCONSIN SECTION

At the regular meeting of the Section, held on April 11, T. Svedberg spoke on "Recent Advances in Colloid Chemistry."

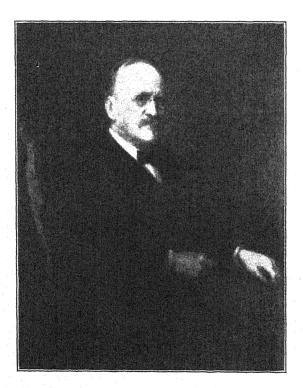
"Nitrogen: A Theme with Variations," was the subject of the address delivered by Lauder W. Jones, of the depertment of chemistry, Princeton University, on April 18, before the Section.

On May 9, E. C. Franklin, President of the American Chemical Society, gave his lecture on "The Ammonia System of Compounds," before the meeting of the members.

FARRINGTON DANIELS, Secretary

#### DECEASED

William Brady, 7642 Marquette Ave., Chicago, Ill. Died, April 26, 1923. John F. McBride, 340 South Ritter Ave., Indianapolis, Ind. Died, March 5, 1923.



Edward Williams Morley

## EDWARD WILLIAMS MORLEY

## 1838-1923

Edward Williams Morley, son of Rev. S. B. and Anna C. (Treat) Morley, was born in Newark, New Jersey, on January 29, 1838. Soon after his birth his parents moved to Hartford, Conn., where they lived until 1851, when his father was called to the pastorate of the First Congregational Church in Attleboro, Massachusetts. A severe illness in early boyhood left such effects on the young Edward that his preparatory studies were carried on with difficulty and for the most part at home under the tutelage of his father. In 1857, the family moved to Williamstown, Massachusetts, for the purpose of putting the sons, of which there were three, through Williams College, the Alma Mater of the father. Edward expected to enter the Freshman class, but the college authorities found him well qualified for the Sophomore class, in which he was duly enrolled. He graduated in 1860, and then entered Andover Theological Seminary, from which he graduated in 1864.

His health was still poor so that he did not feel able to undertake the duties of a minister, but spent the year 1864–5 in the service of the Sanitary Commission—the civil war being then in progress—in charge of their Station at Fort Monroe, Virginia. The next year he spent in study, and in 1866 read his first paper before the American Association for the Advancement of Science on "The Latitude of the Williams College Observatory." During the years 1866–1868 he was teaching in the South Berkshire Academy at Marlboro, Massachusetts. The ill health which had been troubling him for so long now having passed away, he sought and found an opportunity to preach at Twinsburg, Ohio, and almost at the same time was offered a professorship of Natural History and Chemistry in Western Reserve College at Hudson, Ohio, which he accepted. Just before taking up the duties of this new position he married Miss Isabella E. Birdsall of West Winsted, Conn., who was then residing at Hillsdale, New York.

At first Professor Morley was obliged to give instruction in most of the sciences, but his chief interest was in chemistry and he at once had a small room fitted up as a laboratory where, as one of the early catalogs states: "The class perform under the guidance of the professor all those experiments which are suitable for them, while those which demand more experience are performed for the class by the teacher." A course in quantitative analysis was also given at this early date.

Professor Morley was always an indefatigable worker. Later in life he remarked that up to the time of his first vacation in 1895 he had always considered 14 hours a fair day's work. During his first 10 years at Hudson he published 5 papers on various subjects besides doing a good deal of

¹ Proc., Am. Assoc. Adv. Sci., 1866, 384.

outside analytical work. In 1873 he also took on the Professorship of Chemistry and Toxicology in the Cleveland Medical School, which necessitated his spending considerable time going back and forth to Cleveland. This position he resigned in 1888, after he had been in Cleveland some vears. In 1878 he became interested in studying the variation of the oxygen content of the atmosphere and spent three years working on this subject. He determined the proportion of oxygen in the air from various parts of the globe or, where samples could not well be sent to him, analyses were made by chemists on the spot. In 1880 he determined the oxygen content of the air on 110 consecutive days in order to test the so-called Loomis-Morley hypothesis, according to which deficiency of oxygen was supposed to occur at times of high barometric pressure, due to downward currents bringing air from high altitudes to the surface of the earth. He summed up his results in the following words: "The theory that deficiencies in the amount of oxygen in the atmosphere are caused by the descent of air from an elevation fairly well agrees with the facts."² During the course of this work he devised and constructed a new form of precision eudiometer for the rapid determination of oxygen in air.

In 1882 Western Reserve College was moved to Cleveland and was thereafter known as Adelbert College of Western Reserve University. During this period Professor Morley served on the building committee and was one of its most active members, taking a great interest in the establishment of the college in its new quarters. As soon as he became settled in Cleveland he began the magnum opus of his life: "On the Densities of Oxygen and Hydrogen and the Ratio in which They Combine." He was occupied with this for 11 years and had it ready for publication in 1895. It appeared as "Smithsonian Contribution to Knowledge," No. 980 and was also printed in German in the Zeitschrift für physikalische Chemie, 20 (1896). This research at once gave him a world-wide reputation as a scientist of the first rank. In it one sees his remarkable insight into the fundamental nature of the problem, his great skill in devising and manipulating apparatus, his precision of measurement, and his great patience and perseverance in overcoming obstacles at times seemingly insurmountable. It is a remarkable tribute to his work that now, after nearly 30 years, the accepted values of most of the quantities, which are the averages of the best recent work in this field, are practically identical with those found by him.³

This research affords an excellent example of the thoroughness of Professor Morley's work and the care which he took to avoid unconscious bias. It consisted of three parts, each supplying an independent basis

² His principal papers on this subject are: On a Possible Cause of Variation in the Proportion of Oxygen in the Air, Am. J. Sci. [3] 18, 168 (1879), and [3] 22, 417, 429 (1881); Methods for Accurate and Rapid Analyses of Air, Am. Chem. J., 3, 275 (1881).

³ As to the density of oxygen, see the summary by Moles, quoted by the Committee on Atomic Weights for this year, This Journal, 45, 566 (1923).

for calculating the ratio by weight in which hydrogen and oxygen combine. (a) Hydrogen was weighed and then the amount of oxygen with which it combined was weighed. (b) The weight of the water formed from the weighed quantities of hydrogen and oxygen was also determined. Several sets of determinations were carried out, and the final calculations of the ratio were not made until all of them were finished. (c) The densities of hydrogen and oxygen were determined and then the ratio by volume in which these gases combine was found; then from these data were calculated the ratios by weight. These last calculations were not made, however, until after the work had been accepted for publication by the Smithsonian Institution. After that, Professor Morley went to Washington, completed the calculations, and only then learned that the third series agreed with the first two to within less than 1 part in 10,000. As he remarked in one of his papers, "The scientific conscience is rather rigorous."

Many other papers published by Professor Morley during or after this period were the results of work bearing on the research we have just been discussing as, for example, "On the amount of moisture remaining in a gas after drying with sulfuric acid," 4 "One the Amount of Moisture Remaining in a Gas after Drying with Phosphorus Pentoxide," 5 and "On the Vapor Tension of Mercury at Ordinary Temperatures."

Professor Morley had a remarkably versatile mind which embraced with equal ease any one of the physical sciences. His knowledge of mathematics and astronomy was greater than that of many devotees of those sciences, and the physicists considered him as one of their own. At the same time that he was carrying on the work on oxygen and hydrogen he was also collaborating with Professor Michelson in developing the interferometer, an instrument for measuring lengths in terms of the wave lengths of light. They used this instrument to determine the relative motion of the earth and the luminiferous ether.7 A little later, with Professor W. A. Rogers he used it for measuring the expansion of metallic bars.8 In 1904 he again took up the ether drift experiments with Professor D. C. Miller⁹ under improved conditions, but still found that the effect, if any, was much less than expected according to the Newtonian theory. This of course has brought these experiments into prominence again since the Einstein theory has appeared, and Professor Miller has been repeating them at the Mount Wilson Observatory. Previous to this he and Professor Miller had used a similar apparatus in experimenting with the velocity of light in a magnetic field. 10 They also collaborated on experiments to determine the thermal expansion of certain gases, as air, nitrogen, oxy-

⁴ Am. J. Sci., [3] 30, 140 (1885).

⁵ Ibid., [3] 34, 199 (1887). See also This Journal, 26, 1171 (1904).

⁶ Proc. Am. Assoc. Adv. Sci., 1890, 91, and also Am. J. Sci., [4] 18, 83 (1904).

 ⁷ Am. J. Sci., [3] 34, 333 (1887).
 ⁸ Phys. Rev., 4, 1, 106 (1897).
 ⁹ Phil. Mag., [6] 9, 669, 680 (1805).
 ¹⁰ Phys. Rev., 7, 283 (1898).

gen and carbon dioxide. Unfortunately, these papers were never published, only an abstract of them appearing in the Proceedings of the American Association for the Advancement of Science.¹¹

In connection with these last experiments, Professor Morley devised a new form of differential manometer by which differences of gaseous pressure down to 0.0001 mm. of mercury could be measured. He developed another type of this manometer in collaboration with Mr. C. F. Brush, 12 with whom he also carried on a series of experiments on "The Conduction of Heat Through Water Vapor." 13

During the Hudson period, Professor Morley was sorely put to it to find ways and means to supply his needs for apparatus and books, for the college was able to purchase only what few things were indispensable for the student laboratory. He early realized the need of a good library for the proper prosecution of his research and, therefore, welcomed the opportunity of teaching in the Medical School, for that together with what outside analytical work he could do enabled him to buy the apparatus he needed and gradually accumulate a library. By the time he had finished the research on oxygen and hydrogen he possessed one of the most complete libraries of journals on pure chemistry, including full sets of the early ones in English, French and German, to be found in the United States. He also took the Journal of the Russian Physico-chemical Society for a time and learned to read Russian, so as to be able to follow the work in that country along the line of his research. After his retirement from active teaching in 1906, the college purchased this library and it is now housed in the new chemical laboratory, built in 1908-1909, for which he drew plans, and which is known as the Morley Chemical Laboratory.

Professor Morley with all of his greatness was by disposition of a most retiring and modest nature, almost too much so for his own good, as he was but little known outside the ranks of chemists and physicists. He could not bring himself to make the first move in approaching strangers, but once having formed an acquaintance he became most cordial and companionable. He enjoyed in his own quiet way the recognition and honors which came to him after the completion of his work on oxygen and hydrogen. As he expressed it to his classmates of Williams at their fiftieth anniversary, "Teaching has not absorbed all my time and strength, and I have done some pieces of scientific work which are held in good esteem, but these are mostly too technical to be described or even named here." The honors which came to him he speaks of thus: "The degree of LL.D. has been given me by three colleges, one of which was our Alma Mater (the others were Western Reserve and Lafavette, and in 1912 he received it also from the University of Pittsburgh), the degree of Ph.D. by one (Wooster), and the Doctorate of Science by Yale. I am a member of the Na-

¹¹ Proc. Am. Assoc. Adv. Sci., 1897, 123. 
¹² Am. J. Sci., [4] 13, 455 (1902).

¹⁸ Reports Brit. Assoc. Advan. Sci., 1901, p. 525.

tional Academy of Sciences, and have been President of the American Association for the Advancement of Science, and of the American Chemical Society, of which latter I am the only American honorary member. The Royal Institution of London has made me an honorary member. The Chemical Society of the same city has made me a Foreign Member, and the British Association for the Advancement of Science has made me a Corresponding Member." Besides these, under the Harrison administration he was one of the 4 members at large of the committee to receive the United States Prototype Metric Standards at the White House. 1901 he was sent to Paris as the American delegate to the General Conference on International Weights and Measures. He was awarded the following medals: the Sir Humphrey Davy Medal by the Royal Society of London in 1907, the Elliot Cresson Medal by the Franklin Institute of Philadelphia in 1912 and the Willard Gibbs Medal by the Chicago Section of the American Chemical Society in 1917. In 1912 he was Honorary President of the 8th International Congress of Applied Chemistry, and he was a member or fellow of many learned societies in this country and abroad.14 He goes on to say, "I have declined some attractive calls to other fields of work, and so my life has contained few incidents of interest."

"My health has been such as to occasion more care and solicitude than in the case of most, but I have been kept from work by illness not more than eight weeks in the forty years of my work as a teacher." He possessed remarkable vitality, however, which was a great factor in enabling him to finish successfully so many tasks; but no constitution could withstand indefinitely the strain of long hours and hard work, which he constantly imposed upon himself. In 1895 his strength gave out and he was compelled to rest. The college authorities granted him a year's leave of absence, the only one during his teaching experience, and he spent it with Mrs. Morley in recuperation and travel abroad. After his return in 1896 he was given additional assistance and in 1898 the Trustees voted to relieve him of as much teaching as he was willing to relinquish so that he could give more time to research. He chose, however, to retain the courses in general chemistry and in quantitative analysis, and he continued to teach these until he retired as Professor Emeritus in 1906.

Professor Morley had a remarkably retentive mind, so that practically everything which he read was stored in his memory, whence it could be drawn whenever needed. He not only possessed great clarity of expression in writing and speaking but, what is rarer, he had the ability to present scientific matters so that they were interesting to the layman. His public

¹⁴ The following are the societies not mentioned in the text of which he was a member: The American Academy of Arts and Sciences of Boston, American Philosophical Society, Washington Academy of Science, Astronomical and Astrophysical Society of America, German Chemical Society, French Physical Society.

lectures on such subjects as the ether-drift experiments were always well attended, and he held the interest of his audience to the very end.

Next after research he enjoyed exercising his skill on difficult chemical analyses, and during his last years in Cleveland he analyzed many complex minerals for his friend and colleague, Professor H. P. Cushing, who spent a portion of his time with the New York Geological Survey. This sort of work he continued as a pastime after he retired, and his last published paper was in collaboration with Professor Joseph P. Iddings on "Contributions to the Petrography of Java and Celebes."¹⁵

From what has been said it is seen that Professor Morley was a man of remarkable versatility. His brother says of him, "He would easily have made a great theologian. He was surpassed by none and equalled by few in his knowledge of Greek and Hebrew. He would have been eminent in mathematics, astronomy or the humanities. He had a broad knowledge and wonderful appreciation of literature and music, both of which he cultivated to the end of his life." He was a really good amateur musician. He played the chapel organ in the early days at Hudson and at Cleveland took an active interest in the musical life of the College. After he retired this versatility helped him greatly in getting the most enjoyment out of his declining years. I quote again from his letter to his classmates: "In 1906, after teaching just forty years, I retired, hoping by timely rest from hard work, to retain a fair degree of health and good spirits and power of enjoyment. I built a house and a small laboratory in West Hartford, Conn., and we are living there, seeming to find as much enjoyment as at any time in our lives." He also took a great deal of pleasure in out-of-door life, as in the growing of gladioli, using his camera and touring New England in his automobile, which he always drove himself. Only last summer he and Mrs. Morley, whose death preceded his by only a few months, took a trip into Northern Mass, and Vermont in their automobile.

Professor Morley was taken to the Hartford Hospital for an operation on January 21. Another operation was found to be necessary about three weeks later, which was not serious and from which he was expected to recover. Unexpected complications, however, set in and carried him off suddenly on February 24, just a short time after his eighty-fifth birthday. He is buried in Pittsfield, Massachusetts, where his father and mother are also buried.

He lived to a ripe old age, therefore, and it is a pleasure to know that his last years were filled with so much that was pleasant. The work of his earlier years remains as a lasting memorial of his genius. His long teaching service endeared him to several generations of students, and his colleagues and scientific friends will ever cherish his memory for his high ideals, wise counsel and unselfish service.

OLIN FREEMAN TOWER

¹⁵ J. Geol., 23, 231 (1915).

## Proceedings

## COUNCIL

Dr. E. C. Franklin, president of the American Chemical Society, appointed Dr. Arthur D. Little, of Brookline, Mass., as the Society's representative at the inauguration of Dr. Samuel Wesley Stratton as president of the Massachusetts Institute of Technology, held on June 11, 1923.

## MEMBERS ELECTED BETWEEN MAY 15 AND JUNE 15, 1923

Adams, Israel S., Pennsburg, Pa. Bird, Emerson Wheat, 708 Atlantic Ave., Collingswood, N. J. Bird, L. C., 2416 A. Grove Ave., Richmond, Va. Corey, U. S. Naval Medical School, Washington, D. C. Cottringer, Paul, 608 W. Larkin St., Midland, Mich. Courtney, Thos. E., 64 Highland Ave., Cambridge, Mass. Crandell, Dean De F., Arnold House, Oakfield, N. Y. Davis, L. I., Food & Drug Division State Board of Health, Austin, Texas. Davis, Noah S., Jr., Deephaven Camp, Ashland, N. Y. De Frates, Joseph S., 125 Harvard Ave., Collingswood, N. J. Di Monaco, Peter Alexander, 19 Henchman St., Boston, 16, Mass Dressel, Gravton F., Frankford, Michigan. Duckers, Grace E., 112 West Union Ave., Bound Brook, N. J. Dvorak, Joseph, 3577 East 142nd St., Cleveland, Ohio. Ebaugh, Frank Wright, Tulane University, New Orleans, La. Egner, Hans, Experimentalfeltet, Sweden. Emerson, Oliver H., Hawaiian Volcano Observatory, Hilo, Hawaii. Etzold, F. O., Overlook Terrace, Leonia, N. J. Feld, Joseph M., 1412 Washington Ave., New York City. Ford, Aubrey E., 349 4th Ave., Huntington, W. Va. Francisco, G. C., Jr., 1016 N. Zangs Blvd., Dallas, Texas. Frank, Samuel, 173 Henry St., New York City. Frazier, M. Josephine, Puente, California. Fruehan, August, 60 Lenox St., Uniontown, Pa. Fuchs, F. E. 38 Forest Ave., Caldwell, N. J. Gahs, Lockered S., 1758 Gorsuch Ave., Baltimore, Md. Gerth, Max M., 5248 So. Honore St., Chicago, Ill. Glenn, Miltiades L., Box 408, Wesleyville. Pa. Goodman, Jas. G., 400 S. Main St., Jersey Shore, Pa. Harding, Reginald, 130 Webster Ave., Syracuse, N. Y. Harkins, Frank B., Oficina Delaware, Faltal, Chile, South America. Heege, Frederick F., 3218 W. 52nd St., Cleveland, Ohio. Herting, G. Claire, 22 High St., Pottstown, Pa. Honig, P., 47 Julianastraat 47, Rijswijk, Z. H., Holland Howard, Fred A., Old Colony Ave., Wollaston, Mass. Hyde, Harvey W., 112 River St., Watertown, N. Y. Ingmanson, John H., 316 W. 95th St., New York City. Jablons, Benjamin, 498 West End Ave., New York City. Joachim, Herman L., P. O. Box 768, Bogalusa, La. Knowles, John T., 7337 Eberhart Ave., Chicago, Ill. Kunhauser, Frank, 67 Starck Industry, Kaznov n Plane, Czechoslovakia. Livshis, Laura Jane, 2910 Logan Blvd., Chicago, Ill. Lucas, G. H. W., Chem. Lab., University of Toronto, Toronto, Ont., Canada. Mann, Wm. A., 6043 Kimbark Ave., Chicago, Ill. Marshall, Morris D., 15 Idlewild St., Allston, Mass. Mason, Miss Inez D., Isabella Thoburn College, Lucknow, India. Maxwell, Mildred E., 28 Corwin Ave., Zanesville, Ohio. McLachlan, N. E., 408 South 12th East, Salt Lake City, Utah,

Moran, James J., 610 Wood St., Vineland, N. J.

Nickowitz, Max N., Dupont Fabrikoid Co., Fairfield, Conn.

Oden, Sven L. A., Oorganiska Laboratoriet, Kgl Tekniska Hogskolan, Stockholm, Sweden.

O'Grady, Thomas J., New York Lubricating Oil Co., 116 Broad St., New York City.

Parkhurst, Reginald B., 99 Leighton St., Lynn, Mass.

Parry, V. F., 6941 Meade St., Pittsburgh, Pa.

Pusateri, Michael A., 1111 N. Central Ave., Baltimore, Md.

Roehner, Theodore G., Willow Ave., Hempstead, N. Y.

Shack, Louis Mark, 104 Providence St., Worcester, Mass.

Smith, Charles S., Box 221, Elkland, Pa.

Smith, William O., Thaw Hall, University of Pittsburgh, Pittsburgh, Pa.

Spedding, F. H., 917 Greenwood Ave., Ann Arbor, Mich.

Sterrett, M. Brown, 3228 6th Ave., Beaver Falls, Pa.

von Isakovics, Mary Upshur, Monticello, N. Y.

Watson, George W., Union Malleable Iron Co., East Moline, Ill.

Westgate: Ralph S., 23 Vine St., c/o E. R. Squibb & Sons, Brooklyn N. Y.

Wickes, Eliphalet, c/o Mr. R. H. Cory, Dana Place, Englewood, N. J.

Wochele, H. J., 11909 Saywell, Cleveland, Ohio.

Wolff, William A., 230 East 26th St., New York City.

Woodward, Gladys E., 194 Warrenton Ave., Hartford, Conn.

Yung, Chi Chao, 1110 Wertland St., Charlottesville, Va. Zergiebel, C. P., 417 Waldron St., W. Lafayette, Indiana.

#### CORPORATION MEMBER

Joseph H. Wallace & Co., Temple Court Building, New York City.

## MEETINGS OF THE SECTIONS

(Full reports of all meetings should be sent to Secretary Charles I., Parsons, 1709 G St., N. W., Washington, D. C.)

#### AMES SECTION

At the business meeting of the Section, held on June 6, the following officers were elected for the coming year: Anson Hayes, chairman; V. E. Nelson, vice chairman; R. B. Waite, secretary-treasurer; and Henry Hilman, councilor.

R. B. WAITE, Secretary

## ARKANSAS SECTION

The spring meeting of the Section was held on June 12, when Edgar F. Smith, provost emeritus, University of Pennsylvania, addressed the members.

The following officers for 1923-1924, have been elected by the Section: J. W. Johnson, chairman; G. W. Roark, Jr., vice chairman; J. W. Read, secretary; H. G. Lewis, treasurer; and Harrison Hale, councilor.

J. W. Read, Secretary

## CHICAGO SECTION

On June 14, Frank C. Whitmore, of Northwestern University, addressed the Section, his subject being "The Human Side of Mercury." The usual group meetings were held after the address of the evening.

Lee F. Supple, Secretary

## CINCINNATI SECTION

The following officers have been elected by the Section: A. P. Matthews, chairman; Thos. R. Midgely, first vice chairman; Julius Greyer, second vice chairman; Geo. K. Elliott, trustee; A. O. Snoddy, secretary-treasurer; and A. B. Davis, Martin Fischer and C. P. Long, councilors.

A. O. Snoddy, Secretary

## CLEVELAND SECTION

The second annual spring meeting of the Section was held in Cleveland on May 23, in conjunction with adjacent Sections. Various excursions to industrial plants were conducted during the day. The chief speaker at the evening meeting was H. H. Dow, president of the Dow Chemical Co., Midland, Mich., whose subject was "Business Opportunities in Japan."

H. S. Booth, Secretary

## CORNELL SECTION

The following officers for 1923-1924 have been elected by the Section: M. L. Nichols, chairman; F. R. Georgia, vice chairman; C. W. Mason, secretary-treasurer; F. H. Rhodes and G. R. Gillette, executive committee.

C. W. Mason, Secretary

### DETROIT SECTION

The Section held a joint meeting, on May 24, with the chemical and bacteriological section of the American Water Works Association, at Detroit, when the following program was presented: "The Hardness of American Municipal Water Supplies," by W. D. Collins, of the U. S. Geological Survey, Washington, D. C.; "The Physiological Effect of the Mineral Content of Drinking Water," by E. S. Chase, of Metcalf & Eddy, Boston, Mass., and H. C. Hamilton, of Parke-Davis Company; "Corrosion in Hot Water Systems," by C. R. Texter, Mellon Institute, Pittsburgh, Pa.; "The Removal of Dissolved Gases from Water," by J. R. McDermet, of the Elliot Company, Jeannette, Pa.; and "Zeolite Softening of Boiler Feed Water," by S. T. Powell, of Baltimore County Water & Electric Co., Baltimore, Md.

#### ERIE SECTION

The regular monthly meeting of the Section occurred on June 11, when H. T. Clarke, of the Eastman Kodak Company, addressed the members on the subject of "Research Organic Chemicals."

M. A. Krimmel, Secretary

#### LEHIGH VALLEY SECTION

The annual picnic of the section was held on June 2, at Saylor's Lake, Saylorsburg, Pa.

R. H. Bogue, Secretary

## LOUISIANA SECTION

On June 1, Edgar F. Smith, of the University of Pennsylvania, addressed the meeting of the Section, his subject being "Early Organic Chemistry in the United States."

At the meeting of the Section, held on June 15, Robert Glenk, curator of the State Museum, spoke on "Some Unfamiliar Resources of Louisiana."

H. R. STEVENS, Secretary

## MARYLAND SECTION

A joint meeting by the local Section with the Baltimore Section of the American Society of Mechanical Engineers was held on May 25, when E. B. Miller, of the Davison Chemical Company, spoke on "Refining and Recovery of Petroleum Oils by Silica Gel."

ADOLPH HARVITT, Secretary

#### MIDLAND SECTION

The 17th meeting of the Section occurred on March 29. H. H. Dow spoke on "Chemical Industries of the Pacific Coast and Japan," and C. H. Wagner, of the General Ceramics Company, gave an illustrated talk on "The Manufacture of Chemical Stoneware."

The 18th meeting was held on April 27, when E. C. Franklin, president of the American Chemical Society, gave his address on "The Ammonia System of Compounds."

The following officers for 1923-1924 have been elected: Ivan F. Harlow, chairman; Ross T. Sanford, vice chairman; John A. Gann, secretary-treasurer; William J. Hale, councilor; Thomas Griswold, Chester Kennedy and Paul Cottringer, directors.

JOHN A. GANN, Secretary

## NASHVILLE SECTION

At the meeting of the Section, held on May 25, Herman Schlundt, of the University of Missouri, spoke on "Energy of the Atom."

H. A. Webb, Secretary

## NEW YORK SECTION

The following program upon the general subject of "Chemistry in the Serivce of Railroading," was presented on May 4: "Some Problems Confronting the Railroad Chemist," by M. E. McDonnell, chief chemist of the Pennsylvania Railroad System; "Fire Hazards in Freight Transportation," by C. P. Beistle, chief chemist of the Bureau of Safe Transportation of Explosives; and a discussion of these papers by H. E. Smith, engineer of tests of the New York Central Lines.

At the meeting held on June 8, the program was upon the general subject of "Hafnium and Other Rare or Suspected Elements. The following papers were given: "Hafnium, its Discovery, Occurrence and Mineralogical Relations," by G. F. Kunz, president of the New York Mineralogical Club; "Undiscovered Elements," by R. B. Moore, of the Dorr Company; and "Zirconium and Some of its Complex Salts," by F. C. Nonamaker, of the Welsbach Co.

B. T. Brooks, Secretary

#### NORTHEASTERN SECTION

The 186th regular meeting of the Section occurred on June 1, at Worcester, Mass. There was an inspection of the Norton Company plant at Worcester in the afternoon, and in the evening the following papers were presented: "Characteristics of Artificial Abrasives," by L. E. Saunders; "Technical Control in the Manufacture of Grinding Wheels," by M. F. Beecher; "The Art of Grinding," by J. C. Spence; and "Electric Furnace Products as Refractory Materials," by M. R. Kirkpatrick.

E. B. MILLARD, Secretary

## OMAHA SECTION

The regular meeting of the Section was held on June 5. The subject of the evening was "The Function of the Chemist in Railroad Operation," discussed by Wm. G. Haynes and R. W. Savidge, of the Union Pacific Railroad Company.

R. N. PERKINS, Secretary

#### OREGON SECTION

On May 25, E. C. Franklin, president of the American Chemical Society, addressed the members of the Section, his subject being "The Ammonia System of Compounds."

F. L. SHINN, Secretary

### PHILADELPHIA SECTION

The annual outing of the Section occurred on June 14, at the Woodbury Country Club, Woodbury, N. J.

J. Howard Graham, Secretary

## PITTSBURGH SECTION

The annual picnic of the Section was held on June 16 at "The Pines," near Pittsburgh, Pa. Various kinds of outdoor entertainment were given.

E. S. STATELER, Secretary

#### PUGET SOUND SECTION

At the meeting of the Section, on May 24, E. C. Franklin, president of the American Chemical Society, spoke on "The Ammonia System of Compounds."

R. W. Ellison, Secretary

#### RHODE ISLAND SECTION

On May 25, Charles James spoke to the members of the Section, his subject being "Rarer Metals, Their Preparation and Commercial Application."

The annual outing of the Section was held on June 9, at Fairbanks Farm, Greene, R. I.

NELSON BARLOW, Secretary

#### ROCHESTER SECTION

The 156th meeting of the Section occurred on May 21, when John R. Murlin, head of the department of vital economics, University of Rochester, spoke on "Recent Progress in the Extraction and Purification of Insulin."

EARLE R. BILLINGS, Secretary

## SACRAMENTO SECTION

On May 19, the members of the Section joined in an inspection of Sacremento's water filtration plant.

J. H. Norton, Secretary

#### SAINT LOUIS SECTION

At the regular monthly meeting of the Section, held on June 4, Norman C. Hill, of the Monsanto Chemical Works, gave a paper on "The manufacture of Sulfuric Acid."

H. A. CARLTON, Secretary

## SAVANNAH SECTION

On the night of March 30, George P. Shingler addressed the Section, his subject being "A New and Safe Fumigant for Fumigating Ships."

HERBERT P. STRACK, Secretary

## SOUTHERN CALIFORNIA SECTION

The regular meeting of the Section was held on May 24, with the following program: "Some Fundamental Problems in Biological Chemistry," by I. Grageroff; "The Chemical Nature of Some Physiological Products," by H. L. White; and "The Relation of Chemistry to Medicine from the Standpoint of the Bacteriologist," by M. C. Terry.

At this meeting, the following officers for the Section were elected: Walter A. Schmidt, president; W. C. Morgan, vice president; Mark Walker, secretary; C. J. Marvin, treasurer; and S. J. Bates, H. L. Payne and E. R. Miller, councilors.

MARK WALKER, Secretary

#### TOLEDO SECTION

The Section held a meeting on June 7, when G. E. Harter, of The Ransom & Randolph Company discussed the subject, "Foods that Feed and Foods that Kill."

GUY E. VAN SICKLE, Secretary

## UNIVERSITY OF MICHIGAN SECTION

On May 24, G. G. Brown addressed the members of the Section, his subject being "The Chemistry of an Automobile Engine."

C. C. Meloche, Secretary

## WESTERN NEW YORK SECTION

The last meeting of the season was held on May 29. There was a talk by W. H. Watkins, and a scientific film on the "Einstein Theory of Relativity" was shown.

R. W. HESS, Secretary

## WISCONSIN SECTION

At the 126th meeting of the Section, held on June 6, L. V. Redman, of Chicago, Ill., spoke on "The Story of Redmanol." FARRINGTON DANIELS, Secretary

DECEASED

Carl Bache-Wiig, Portland, Maine. Died, August 17, 1922. Emil Homburg, 104 West Clifton Ave., Cincinnati, Ohio. Ralph S. Potter, 29 East 21st St., New York City.

## Proceedings

## COUNCIL

President E. C. Franklin has appointed Mr. H. E. Howe the representative of the American Chemical Society on the Alcohol Trade Advisory Committee.

Past President Edgar F. Smith has been appointed to represent the American Chemical Society at the Joseph Leidy Commemorative Meeting to be held in Philadelphia on December 6, 1923.

## MEMBERS ELECTED BETWEEN JUNE 15 AND JULY 15, 1923

Arrhenius, Olaf Wilhelm, Gamla Haga, Stockholm, Sweden.

Brice, Paul B., 1431 Chesapeak Road, Camden, N. J.

Butler, George Herbert, 2 Forest Road, Bulwer Park, Durban Natal, South Africa.

Choquette, Paul J., 89 Butterfield St., Lowell, Mass.

Ehret, William F., 1732 Norman St., Evergreen, L. I., N. Y.

Erickson, Ernst, 659 Madison Ave., York, Pa.

Fujita, Eitaro, Kamichoja-Machi Senbon Nishi-iru, Kyoto, Japan.

Hall, Charles B., 2194 Ambleside Drive, Cleveland, Ohio.

Hashi, K., College of Technological Chem., Kyoto Imperial University, Kyoto, Japan.

Kao, C. H., 1324 W. Dayton St., Madison, Wis.

Kwan, Pao-Chun, Herrn Direcktor Langen Maschinenfabrick Grevenbroich, Grevenbroich, Bei Coln Niederrhein, Germany.

Lines, George O., 735 Cass St., Milwaukee, Wis.

Marzano, Rev. C., 1101 Bay St., Rosebank, S. I., N. Y.

Munning, August P., Matawan, N. J.

Newell, I. Laird, 12 Crescent St., Middletown, Conn.

Nierenstein, Maximilian, Chemistry Department, University of Bristol, Bristol, England.

Peck, Theodore A., Box 1542, St. Louis, Mo.

Potter, Truman Squire, 5515 Woodlawn Ave., Chicago, Ill.

Rager, Carroll A., 1617 Race St., Philadelphia, Pa.

Silhavy, George F., 226 Ward St., Saginaw, Michigan.

Stewart, Francis S., 418 Florence St., Palo Alto, Cal.

Stewart, James Kirby, Martinez, California.

Trossman, Henry, 606 Roosevelt Blvd., Philadelphia, Pa.

## MEETINGS OF THE SECTIONS

(Full reports of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

## INDIANA SECTION

At the regular monthly meeting of the Section, held on May 11, the following members were elected to office for the current year: H. E. Jordan, chairman; C. B. Edward, vice-chairman; H. A. Shonle, secretary-treasurer; E. W. McCullough, John R. Kuebler and Neil M. Waterbury, executive committee.

HORACE A. SHONLE, Secretary

#### PHILADELPHIA SECTION

The newly elected officers of the Section are as follows: J. Howard Graham, chairman; Elmer C. Bertolet, secretary-treasurer.

ELMER C. BERTOLET, Secretary

## RHODE ISLAND SECTION

At the annual meeting of the Section, the following officers for 1923-1924 were elected: Samuel T. Arnold, chairman; Nelson Barlow, vice-chairman; Lucius A. Bigelow, secretary-treasurer.

Lucius A. Biorlow, Secretary

#### TOLEDO SECTION

On June 7, the following officers for 1923 were elected: T. E. Moore, chairman; G. H. Anderson, vice-chairman; W. B. Holmes, councilor; and W. E. Ruth, secretary-treasurer.

W. E. Ruth, Secretary

#### WESTERN NEW YORK SECTION

At the annual meeting of the Section, the following officers for 1923 were elected: G. P. Fuller, chairman; J. A. Handy, first vice-chairman; F. L. Koethen, second vice-chairman; R. W. Hess, secretary; R. A. Nelson, treasurer; M. J. Ahern, H. N. Gilbert and J. R. MacMillan, executive committee; C. G. Derick, Walter Wallace and A. M. Williamson, councilors.

R. W. Hess, Secretary

#### DECEASED

Bowers, O. C., 2 East Reno Ave., Oklahoma City, Okla. Died, August, 1922. Bush, Donald M., 1135 Russell Ave., Bethlehem, Pa. Died, May 31, 1923. Clam, C. E., California Club, Los Angeles, Cal. Died, May 22, 1923. Cook, Frank C., Bureau of Chemistry, Washington, D. C. Died, June 11, 1923. Judge, Thos. F., Grand Falls, Newfoundland. Died, May, 1922. Katzenstein, Sidney W., Antrim Iron Co., Mancelona, Mich. Died, Dec. 29, 1922.

## NOTICE TO CANDIDATES INTENDING TO APPLY FOR A GRANT FROM THE "VAN'T HOFF FUND" FOR THE AID OF INVESTIGATORS IN THE FIELD OF PURE AND APPLIED CHEMISTRY

According to the regulations of the "Van't Hoff Fund" founded June 28, 1913, persons interested are notified that the foundation located in Amsterdam under the supervision of the Royal Academy of Sciences appropriates, from the income of the fund, annually, before March 1st, allotments to investigators in the field of pure and applied chemistry, who shall have applied for such a grant to the Committee charged with considering the applications and awarding the funds allotted.

At present this Committee is constituted as follows: A. F. Holleman, President; S. Hoogewerff, A. Smits, J. P. Wibaut, Secretary. If desirable the Committee may appoint still other members for one year only, to cooperate in judging the applications.

The names of persons to whom a grant is allowed, will be published. The grantees are requested to send to the Committee copies of papers giving the results of their work; but otherwise they are at liberty to choose the manner of publication, as well as the journal, in which to publish their results, only mentioning the fact, that the research was made with an appropriation from the "Van't Hoff Fund."

The amount available for 1924 is about fourteen hundred Dutch florins. Applications should be mailed registered to: Het bestuur der Koninklyke Akademie van Wetenschappen; bestemd voor de Commissie van het "Van't Hoff-fonds," Trippenhuis, Kloveniersburgwal, te Amsterdam, with a detailed account of the proposed use of the grant, the amount required, and the reasons upon which the candidates ground their claim. They must be received before November 1, 1923.

A. F. HOLLEMAN, President, J. P. Wibaut, Secretary

Amsterdam, the month of June, 1923

# Proceedings

## GENERAL MEETING MINUTES

The Sixty-Sixth General Meeting of the American Chemical Society was held in the Auditorium, Milwaukee, Wisconsin, Monday, September 10, to Friday, September 14, 1923.

Opening addresses were given by Clare H. Hall, Chairman of the Milwaukee Section of the American Chemical Society; Hon. Daniel W. Hoan, Mayor of Milwaukee; Hon. Emmanuel Philipp, President Milwaukee Association of Commerce; and Rev. Albert C. Fox, President Marquette University. Dr. E. C. Franklin responded on behalf of the Society.

Two general addresses were the feature of the Tuesday morning session as follows: Charles F. Burgess, Director, Burgess Laboratories. "Marketing Chemical Discoveries."

Arthur I. Kendall, Dean of the Medical School, Northwestern University. "Bacteria and the Chemist."

The previous custom of having general addresses in the afternoon session was abandoned and instead thereof three special meetings of the more fundamental divisions of Physical and Inorganic Chemistry, Organic Chemistry, and Chemical Education were held with papers especially selected to meet the needs of all chemists present.

On Tuesday evening a complimentary dinner and entertainment was given to the members and guests by the Milwaukee Section. Approximately one thousand sat down to this dinner. The program consisted of songs, dancing, and instrumental music.

On Wednesday at 8 P. M., a reception was held at the Marquette University gymnasium followed by public addresses by Mrs. Thomas G. Winter, President General Federation of Women's Clubs, and the annual address of the President of the Society. President Franklin took as his subject, "Systems of Acids, Bases and Salts." Past President Edgar F. Smith presented the Priestley Medal in absentia to Professor Ira Remsen.

On Thursday evening group dinners and college reunions were held and the members also attended a very interesting and lively amateur boxing contest at the Milwaukee Athletic Club.

A special program consisting of dinners, automobile drives, etc., was arranged for the ladies and a complimentary dinner was given to the wives of the Councilors on Monday evening.

Wednesday and Thursday were otherwise given up wholly to divisional meetings.

The following Divisions and Sections met: Divisions of Agricultural and Food Chemistry, Biological Chemistry, Cellulose Chemistry, Dye Chemistry, Fertilizer Chemistry, Industrial and Engineering Chemistry, Leather Chemistry, Chemistry of Medicinal Products, Organic Chemistry, Petroleum Chemistry, Physical and Inorganic Chemistry, Rubber Chemistry, Sugar Chemistry, Water, Sewage and Sanitation; Sections of Chemical Education, Gas and Fuel Chemistry, and History of Chemistry.

The divisions elected officers as follows:

Division of Agricultural and Food Chemistry: Chairman, C. H. Bailey; Vice-Chairman, E. F. Kohman; Secretary, C. S. Brinton; Executive Committee, G. E. Holm, J. W. Read, R. H. Carr.

Division of Biological Chemistry: Chairman, W. T. Bovie; Secretary, R. A. Dutcher.

DIVISION OF CELLULOSE CHEMISTRY: Chairman, G. J. Esselen, Jr.; Vice-Chairman,

- Louis E. Wise; Secretary-Treasurer, L. F. Hawley; Executive Committee, The Officers ex-officio and Harold Hibbert, A. W. Schorger.
- Division of Due Chemistry: Chairman, W. J. Hale; Vice-Chairman, R. E. Rose; Secretary, R. Norris Shreve; Executive Committee, L. A. Olney, L. F. Johnson.
- Division of Fertilizer Chemistry: Chairman, F. B. Carpenter; Vice-Chairman, R. N. Brackett; Secretary, H. C. Moore; Executive Committee, H. J. Wheeler, C. H. Jones, E. W. Magruder, and A. J. Patten.
- Division of Industrial and Engineering Chemistry: Chairman, D. R. Sperry; Vice-Chairman, W. A. Peters; Secretary, E. M. Billings; Executive Committee, W. K. Lewis, C. E. Davis, E. R. Weidlein, C. S. Miner, C. E. Coates.
- Division of Leather and Gelatin Chemistry: Chairman, John Arthur Wilson; Vice-Chairman, F. P. Veitch; Secretary, Arthur W. Thomas; Executive Committee, I. D. Clarke, L. M. Tolman.
- Division of Chemistry of Medicinal Products: Chairman, E. H. Volwiler; Secretary, H. A. Shonle; Executive Committee, E. B. Carter, Frank O. Taylor.
- DIVISION OF ORGANIC CHEMISTRY: Chairman, R. R. Renshaw; Secretary, J. A. Nieuwland.
- DIVISION OF PETROLEUM CHEMISTRY: Chairman, R. R. Matthews; Vice-Chairman, R. E. Wilson; Secretary, W. A. Gruse; Executive Committee, E. W. Dean, W. F. Faragher.
- Division of Physical and Inorganic Chemistry: Chairman, Graham Edgar; Vice-Chairman, Arthur Hill; Secretary, H. B. Weiser; Executive Committee, R. E. Wilson, G. S. Forbes, A. W. Browne, C. E. Coates, H. Schmidt.
- DIVISION OF RUBBER CHEMISTRY: Chairman, E. B. Spear; Vice-Chairman, C. R. Boggs; Secretary, A. H. Smith; Executive Committee, Winfield Scott, W. B. Wiegand, Ira Williams, L. B. Sebrell, H. B. Pushee.
- DIVISION OF SUGAR CHEMISTRY: Chairman, F. W. Zerban; Vice-Chairman, H. W. Dahlberg; Secretary-Treasurer, Frederick Bates; Executive Committee, C. E. Coates, W. B. Newkirk, J. S. Osborne, H. Z. E. Perkins, M. J. Proffitt, J. R. Withrow.
- Division of Water, Sewage & Sanitation Chemistry: Chairman, W. W. Skinner; Vice-Chairman, F. W. Mohlman; Secretary, F. R. Georgia; Executive Committee, A. L. Fales, A. M. Buswell.

## DIRECTORS' MINUTES

The Directors of the American Chemical Society met in the President's Room at the Hotel Pfister, Milwaukee, Wisconsin, on the evening of September 10, 1923, at 10:30 p. m., following the Council Meeting, with President Franklin in the Chair and Directors W. D. Bancroft, George D. Rosengarten, H. P. Talbot, John E. Teeple, W. R. Whitney, and Charles L. Parsons present.

The rebate to local sections recommended by the Council and appearing in the Council Minutes was approved by the Directors, with the additional proviso that the payments be made to local sections, on rebates received from the dues of New members obtained through them, on a quarterly basis; *i. e.*, on March 1, June 1, September 1, and December 1.

It was moved to approve the rate of \$6.41 per page for composition, make-up, lock-up, and make-ready arrangement by the editor of Chemical Abstracts with the Eschenbach Printing Company for the use of six point type on a seven-point base in the index.

It was voted to make an appropriation to the editor of Chemical Abstracts not exceeding \$975.00 covering the purchase of a safe cabinet for protecting his collective index from fire and for the purchase of a new typewriter for his office.

The Treasurer reported the following transactions since the last Directors' Meeting:

April 23, 1923	Sold \$1000 Brooklyn Rapid Transit 7% Unstamped certifi-	
	cates at 92°/4, General Investments	\$ 926.00
April 23, 1923	Sold \$5000 Brooklyn Rapid Transit 7% Unstamped certifi-	
	cates at 925/8, Morris Loeb Fund	\$4623.75
May 20, 1923	Sold (at maturity) \$20,000 Victory Liberty Loan Bonds, ac-	
	count Temporary Investments.	
May 20, 1923	Sold (at maturity) \$100 Victory Liberty Loan Bond, Priest-	
	ley Memorial Fund.	
June 26, 1923	Called and paid to-day, \$200.00 Federal Land Bank of Hous-	
	ton, 5% 1938 Bonds. Priestley Memorial Fund.	
*,		

It was voted that the Treasurer be authorized to pay from the Priestley Memorial Fund for procuring the Priestley Gold Medal of 1923.

The meeting then adjourned.

CHARLES L. PARSONS, Secretary

## ADVISORY COMMITTEE MINUTES

The Advisory Committee of the American Chemical Society met in the President's room at the Hotel Pfister, Milwaukee, Wisconsin, at 10:00 a. m., Monday, September 10, with President Franklin in the chair and Messrs. Edgar F. Smith, A. M. Comey, H. E. Howe, A. B. Lamb, and C. L. Parsons present.

The Secretary was instructed to proceed along the lines already under way to obtain a coöperative committee between the American Chemical Society, the American Medical Association, and the Society of Bacteriologists and Pathologists with reference to joint action covering the interests of physicians, chemists, bacteriologists, and pathologists in legislation now being presented in certain states. The President was authorized to appoint members from the American Chemical Society to sit on such joint committee, provided the other societies agreed.

It was voted to recommend a rebate to local sections on new members obtained through local sections as outlined in the Council Minutes.

A request having been received from H. W. Gillett for the approval of the Advisory Committee looking toward the use of oxygen in metallurgical processes, the Advisory Committee, after considering the report offered, gave its approval thereto.

It was voted that owing to the inability of the Society to take part actively in the final determination of the candidate for the Perkin Medal, it was inadvisable to make nominations therefor.

A request having been received from the Chairman of the International Critical Tables for the appointment of a successor to Dr. C. E. K. Mees, who had resigned from the editorial board, the President, with the approval of the Advisory Committee, appointed S. C. Lind thereto.

The committee then adjourned.

CHARLES L. PARSONS, Secretary

## EXECUTIVE COMMITTEE MINUTES

The Executive Committee met in the Directors Room of the Auditorium at Milwaukee, Wisconsin, at 2:30 p.m., Tuesday, September 11, 1923, with the following members present: E. C. Franklin, E. J. Crane, J. E. Teeple, George D. Rosengarten, H. E. Howe, and C. L. Parsons.

The rules presented by the Supervisory Committee on Methods of Analysis and referred by the Council to the Executive Committee with power were unanimously approved. The rules can be found printed in the Council Proceedings.

Dr. Wilder D. Bancroft having reported that the Chemical Society has voted in England that papers submitted at any meeting can be published either in the Transactions of the Chemical Society or the Journal of Physical Chemistry, as the author prefers, the Secretary was instructed to modify the announcement sent out on the preliminary and final program regarding Society ownership of papers to read as follows:

All papers presented before the General Meeting, Divisional Meetings, or meetings of local sections are the property of the American Chemical Society unless released by the Society's Editors or by the Editor of the Journal of Physical Chemistry. No paper already offered for publication in another journal should be read. If release is desired, address the editor of the appropriate journal; i. e., H. E. Howe, A. B. Lamb, or W. D. Bancroft.

The committee then adjourned.

CHARLES L. PARSONS, Secretary

## COUNCIL MINUTES

The Council of the American Chemical Society met in the Red Room of the Hotel Pfister, Milwaukee, at 2:30 p. m., Monday, September 10, the meeting continuing, with a short intermission for dinner, until 10:30 p. m. President Franklin was in the Chair and the following Councilors were present:

Ex-Officio.—Wilder D. Bancroft, A. M. Buswell, F. B. Carpenter, Edgar B. Carter, E. J. Crane, G. J. Esselen, Jr., Charles H. Herty, W. F. Hillebrand, J. S. Hughes, Arthur B. Lamb, Ralph R. Matthews, H. A. Noyes, Charles L. Parsons, George D. Rosengarten, Edgar F. Smith, D. R. Sperry, H. P. Talbot, John E. Teeple, W. R. Whitney, John Arthur Wilson, Robert E. Wilson.

Councilors-at-Large.—Roger Adams, A. M. Comey, W. D. Harkins, H. E. Howe, W. Lee Lewis, R. H. McKee.

Local Sections .- Akron, C. W. Bedford (subs. for H. E. Simmons), R. P. Dinsmore. Ames, F. E. Brown (subs. for Henry Gilman). Arkansas, Harrison Hale. Chicago, Herbert N. McCoy, L. V. Redman, W. R. Smith, Ethel M. Terry, Paul Van Cleef, G. L. Wendt, Frank C. Whitmore. Cincinnati, A. W. Broomell (subs. for C. P. Long), A. S. Richardson (subs. for H. J. Morrison). Cleveland, J. D. Morron (subs. for W. R. Veazey). Columbus, James R. Withrow. Connecticut Valley, Joseph S. Chamberlain, C. R. Hoover. Cornell, A. W. Browne. Delaware, Charles L. Reese. Detroit, Adrian Thomas (subs. for H. C. Hamilton). Erie, Paul H. Henkel. Indiana, W. C. Bartholomew (subs. for H. W. Rhodehamel), H. A. Shonle (subs. for F. C. Atkinson). Iowa, Edward Bartow. Lehigh Valley, Eugene C. Bingham (subs. for John T. Little). Lexington, J. S. McHargue (subs. for H. P. Newton). Louisiana, C. E. Coates. Maryland, N. E. Gordon, E. Emmet Reid (subs. for A. E. Marshall). Milwaukee, Robert N. Bauer, C. R. McKee. Minnesota, R. A. Gortner, Charles A. Mann. Nebraska Fred W Upson. New York, Benjamin T. Brooks, Clarke E. Davis, Robert P. Fischelis (subs. for Williams Haynes), Arthur E. Hill (subs. for F. H. Getman), James Kendall, D. B. Keyes (subs. for B. R. Tunison), Sidney D. Kirkpatrick (subs. for H. C. Parmelee), R. R. Renshaw (subs. for C. A. Browne), F. W. Robinson (subs. for David Wesson), Arthur W. Thomas. Northeastern, Geo. L. Coyle, W. C. Durfee, G. S. Forbes, R. T. Haslam (subs. for J. B. Conant), R. W. Neff, James F. Norris, L. A. Pratt, F. G. Stantial (subs. for W. L. Jennings). Northern Indiana, J. A. Nieuwland. Philadelphia, C. S. Brinton (subs. for Jacob S. Goldbaum), Harlan S. Miner, Owen L. Shinn (subs. for Edwin F. Hicks), William Stericker (subs. for F. C. Nonamaker), Walter T. Taggart. Pillsburgh, James O. Handy, Alexander Silverman (subs. for E. W. Tillotson), H. C. P. Weber. Puget Sound. H. V. Tartar (subs. for H. K. Benson). Purdue, E. G. Mahin, Rochester, Erle M. Billings (subs. for H. LeB. Gray), H. T. Clarke. Saint Louis, A. C. Boylston, Charles W. Cuno. Southeast Texas, F. M. Seibert. Syracuse, L. E. Wise. University of Illinois, B. S. Hopkins, S. W. Parr. University of Missouri, Henry D. Hooker, Jr. Virginia, Graham Edgar. Washington, D. C., W. D. Collins, J. W. Sale (subs. for W. W. Skinner), M. X. Sullivan (subs. for R. B. Sosman). Western New York, Walter Wallace. Wisconsin, L. F. Hawley, Victor Lenher.

H. E. Howe, Chairman of the Committee on Garvan Chemical Prizes for secondary schools, outlined the gift of Mr. and Mrs. Francis P. Garvan and the preliminary work and future plans of the Committee as follows:

Shortly after the spring meeting President Franklin appointed a committee consisting of W. D. Bancroft, Charles H. Herty, H. E. Howe, Chairman, and A. H. Williams, Secretary, to organize the work incident to a prize essay contest, made possible by a gift from Mr. and Mrs. F. P. Garvan, as announced in the following letter.

June 1, 1923

"Council of the American Chemical Society Gentlemen:

In order that the youth of our country may have an intelligent appreciation of the vital relation of the development of chemistry to our national defense, to the intensification and purification of industry and agriculture and to the progress of medicine through the "Age of Chemistry" upon which we have entered, and in memory of our daughter, Patricia, Mrs. Garvan and myself tender to you the sum of ten thousand dollars. Six thousand dollars is to be expended by you in awarding in each State six prizes of twenty dollars in gold to the students in all secondary schools, public and private, for the six best essays evidencing an understanding of the importance of chemistry in our national life. The remaining four thousand dollars is to defray the expenses of the contest.

In addition, we have provided for six four-year scholarships in chemistry, or chemical engineering at Yale University or Vassar College, to be awarded by you among the successful contestants in each of the several States. These scholarships will carry five hundred dollars a year and tuition. The choice of subjects, all rules and regulations governing the contests, the awarding of the prizes, and scholarships, et cetera, are to be under your absolute control and direction.

Sincerely yours, Francis P. Garvan"

Upon vote of the Council this gift has been accepted and the following letter of acceptance forwarded by President Franklin.

"August 21, 1923

Mr. Francis P. Garvan 67 Wall Street New York City Dear Mr. Garvan:

On behalf of the American Chemical Society and upon the authorization of its Council it gives me great pleasure to accept the gift of Mrs. Garvan and yourself in memory of your daughter Patricia.

Your plan by which a more extensive interest in chemistry will be engendered has the enthusiastic approval of the Society. I have, therefore, appointed a committee composed of H. E. Howe, Chairman, W. D. Bancroft, Charles H. Herty and Alexander Williams, Jr. (Secretary) to organize and carry forward this work.

Believe me, Sir,

Very sincerely yours, E. C. Franklin, President"

In carrying out the details of the contest the committee has approved and is about to issue a poster announcing the prize contest, this poster to be sent to all secondary schools, both public and private, libraries and other places where its posting will forward the contest. Means have also been provided whereby 10,000 sets of books of five volumes each will be sent gratis to the accredited secondary schools of the country and a large number of sets deposited in libraries, selected with the cooperation of the American Library Association.

Preliminary steps have been taken toward the formation of state committees which will award the prizes in the individual states and a national committee will be formed to award the Scholarships at Yale and Vassar.

A publicity campaign has been formulated and it will soon be time to call upon the various members and local sections of the American Chemical Society to carry forward the very considerable amount of detailed work incident to the successful completion of the project. The committee has reason to believe that a demonstration that this contest can be highly successful and the interest of a large number of boys and girls secured may lead to still greater things for chemistry in this country. It wishes to emphasize that the task in hand is one for which the Society as a whole has a large measure of responsibility and that the committee cannot hope to properly discharge its duties without a large amount of effort being given to the contest by all members of the Society.

A booklet has been prepared which, with the posters, will shortly be sent to high and secondary school principals and professors of chemistry giving details of the contest and the committee urges everyone to be prepared to render such assistance as may be required by perspective contestants.

It was voted to adopt the report and to instruct the Secretary to express the Society's hearty thanks and appreciation to Mr. and Mrs. Garvan for their splendid gift.

Edgar F. Smith presented a report of his conference with the officials of the Allied Chemical and Dye Corporation regarding the \$25,000 prize announced in Proceedings for 1922, page 88.

The following vote was prepared and spread on the minutes and the Secretary was instructed to forward a copy of the same to the Allied Chemical and Dye Corporation:

The American Chemical Society received at its last annual meeting the announcement of a monumental gift for the promotion of chemistry in America—an annual prize of \$25,000, founded by the Allied Chemical and Dye Corporation. The Council reaffirms its acceptance of this gift with deep appreciation of its importance.

The committee to whom this matter was referred having agreed that the name of the prize shall be

## The American Chemical Prize (Founded by the Allied Chemical and Dye Corporation)

the Council heartily concurs in this recommendation. The committee also recommends that the jury of award be a self-perpetuating body consisting of seven members, five of whom shall represent the American Chemical Society and two shall be named by the Allied Chemical and Dye Corporation. This the Council also approves and empowers its committee composed of Edgar F. Smith, Charles F. Chandler, Ira Remsen, Frank P. Venable, and Theodore W. Richards to select the initial five members representing the American Chemical Society.

The Council further approves the following supplemental recommendations of the committee:

The prize shall be awarded annually to that chemist, man or woman, a citizen or a resident of the United States of America at the time, who in a certain year or through a period of years has made a contribution of high merit or in some marked way has promoted the betterment of society through the science of chemistry.

Chemists engaged in any division of their science including the teaching of chemistry shall be cligible for the prize.

The jury of award shall select the recipient of the prize. It shall formulate the rules and regulations governing the award of a prize.

The prize shall be presented at an annual meeting of the American Chemical Society. The recipient of the prize will be expected to receive the prize in person and shall be invited to deliver an address before the Society, his expenses in attendance at the meeting to be defrayed by the Allied Chemical and Dye Corporation.

It was voted to authorize the Section of Chemical Education to form a Division of Chemical Education.

The following new fellowships and continuation of annually awarded fellowships were announced:

The Hammermill Paper Company has given a fellowship of \$1200 to the New York State College of Forestry, to be known as the "Hammermill Fellowship in Pulp and Paper Manufacturing."

The Grasselli Chemical Company has renewed its fellowship for \$750 and scholarship for \$500 in the Massachusetts Institute of Technology.

The du Pont Company has also renewed its fellowship in the Massachusetts Institute of Technology.

The Public Health Institute of Chicago has renewed its twelve \$500 research fellowships in chemistry at Northwestern University, and in order to preserve the time of the fellows for research, the same Institute has made an additional annual appropriation of \$3000 for the support of a special laboratory for the preparation of research intermediates not available on the market.

The National Lime Association has awarded a \$1000 fellowship at the Massachusetts Institute of Technology.

The du Ponts, the National Lime Association, and the Grasselli Chemical Company have renewed their fellowships at the Ohio State University.

A. F. Gallun and Sons have renewed their annual grant of \$5000 for leather chemistry research to Arthur W. Thomas at Columbia University.

The du Pont Company has provided a research fund of \$3600 for research in plasticity at Lafayette College for 1923-24.

The Palm Olive fellowship of \$2000 on the detergent action of soap has been awarded to Paul H. Fall, who will work under Dr. Bancroft at Cornell University.

The Fleischmann Company has renewed its fellowship at the University of Minnesota.

The Stretmann Biscuit Company, of Cincinnati, Ohio, has given a fellowship of

\$1000 to the University of Minnesota for the study of the chemistry involved in the cracker manufacture.

The following resolution presented by Professor E. C. Bingham, Chairman of the Metric System Committee, was adopted:

All articles relating to laboratory tests of procedure published in any of the journals of the American Chemical Society shall contain dimensions expressed metrically. Other equivalents may be added where the author so desires.

The following report of the Editor of Technologic Monographs was read and accepted:

To the President of the American Chemical Society:

During the present year we have been more successful in arranging for the preparation of new monographs than for the delivery of manuscripts, some of which are long overdue.

Three monographs of this series have been published during the year—Glue and Gelatin by Alexander, The Chemistry of Leather Manufacture by Wilson, and Wood Distillation by Hawley. These volumes have been widely and for the most part favorably reviewed.

The manuscript on Coal Carbonization by Porter is expected the last of the year. Corrosion of Alloys by Fink is not yet ready for our reviewers, and the necessity of Braham's going to Europe has delayed work upon his monograph on Cyanamide. Shale Oil by McKee is being revised by the author. Saklatwalla expects to finish his work on Aluminothermic Reduction of Metals at an early date. Waggaman's monograph being prepared without contract, on Phosphoric Acid, Phosphates, and Phosphatic Fertilizers, will be in our hands October 15. G. A. Burrell's manuscript on Extraction of Gasoline from Natural Gas will be ready late this autumn.

During the year contracts have been made for the following monographs: Physical and Chemical Properties of Glass by George W. Morey, due October 1, 1924; Chemistry of the Treatment of Water and Sewage by A. M. Buswell, due September 1, 1924; Chemistry of Wheat Flour by C. H. Bailey, due July 1, 1924; Rare Gases of the Atmosphere by R. B. Moore, due August 1, 1924; Manufacture of Sulfuric Acid by Andrew M. Fairlie, due January 1, 1925; Soluble Silicates by J. G. Vail, due April 1, 1925; Equilibrium between Soluble Salts and their Aqueous Solutions by W. C. Blasdale; Protective Metallic Coatings by H. S. Rawdon, due January 1, 1926. There will be prepared by J. E. Teeple a monograph dealing with the Searles Lake project from a research and chemical engineering viewpoint, but the excitate and title have not yet been chosen. C. R. Hoover will also prepare a monograph on the Materials of Laboratory Construction.

This year the terms of Messrs. C. P. Townsend and C. G. Derick as members of the Board expire and the editor desires to nominate F. C. Zeisberg and W. A. Schmidt as their successors.

Respectfully submitted, H. E. Howe, Editor

The Council elected F. C. Zeisberg and W. A. Schmidt as members of the Board, as recommended.

The following ad interim report of the Finance Committee was accepted:

## INTERIM REPORT OF THE FINANCE COMMITTEE

The budget for 1923 as approved by the Directors anticipated receipts of \$308,400 and expenses of \$311,800. As no one can probably foresee the receipts or expenditures of the Society to an accuracy closer than 1%, this was considered a balanced budget.

At the present time it looks as though the receipts from advertising will be about \$16,000 less than our estimate, and receipts from other sources will be approximately \$9000 more than our estimate giving net receipts for the year of probably \$302,000.

It looks as though expenses for the year will be about \$302,000 or \$303,000, due to various savings in a number of different departments. If these savings all materialize, then, we should expect to have the receipts and expenditures balance within at least \$2000 or \$3000.

The net advertising receipts will be very nearly the same as they were last year. The plans for this year, however, called for a very considerable increase in advertising receipts, and these did not materialize due to changed business conditions.

F. J. METZGER
F. G. ZINSSER
JOHN E. TEEPLE, Chairman

The invitation to hold the Spring Meeting of 1924 in Washington, D. C., was accepted.

The invitation to hold the Fall Meeting of 1924 in Ithaca, N. Y., was accepted.

It was voted that the Council recommend to the Directors that local sections be allowed a rebate of \$5.00 on each new member of the Society and \$2.50 on any former member reinstated in membership, obtained by them and transmitted to the Secretary of the Society by the Secretary of the local section or chairman of their membership committee. It was further recommended that if this vote was approved by the Directors the following rules shall govern:

- 1. Rebates shall apply only on the first payment of new members paying full \$15.00 dues.
- 2. Rebates shall be claimed at time of transmittal of application and shall apply only to applications transmitted to or by the secretary of the local section or the chairman of their membership committee.
- 3. Rebates shall not apply to members resigning in good standing who are reinstated until after a period of two years has elapsed following their resignation.

This motion was approved by the Directors on the following day with the addition of a fourth requirement, namely:

4. Payments of these rebates to local sections shall be made quarterly, on March 1st, June 1st, September 1st, and December 1st.

The Committee on Intersectional Meetings reported progress and was continued until the next meeting.

The Committee on Classified Membership reported progress and was continued until the next meeting.

It was voted to establish a local section with headquarters at State College, Pennsylvania, comprising the counties of Center, Clearfield, Clinton, Union, Mifflin, Huntingdon, Lycoming, and Blair, as soon as the requirements have been met by the chemists petitioning.

On request of the Section of Chemical Education, its committee on Chemical Education, consisting of Neil E. Gordon, B. S. Hopkins, J. R. Kuebler, L. W. Mattern, L. C. Newell, W. D. Richardson, R. E. Rose, Walter Schmidt, W. Segerbloom, and R. E. Swain was made a committee of the Society.

The following rules suggested by the Supervisory Committee on Standard Methods of Analysis were read to the Council, and by the Council referred to the Executive Committee for study and approval. The Executive Committee on the following day took up these rules and unanimously adopted them as the rules of the Society:

RULES RELATING TO COMMITTEES OF THE SOCIETY AND OF ITS DIVISIONS AND SECTIONS HAVING TO DO WITH THE STANDARDIZATION OF METHODS OF ANALYSIS

For earlier rules see Proc. 1910, p. 106, and 1917, p. 97.

- 1. The Supervisory Committee on Standard Methods of Chemical Analysis shall remain as heretofore under the control of the Council but with power to approve or reject reports presented to it, without submitting its decisions to the Council for final action.
- 2. The Supervisory Committee shall consist of a nucleus of five (5) members no one of whom shall be a member of one of the subordinate committees hereinafter referred to unless he be already a member of the nucleus of the Supervisory Committee or become so by appointment. In the latter event he shall cease to be a member of the subordinate committee unless he happens to be its chairman.

In addition, the chairmen of committees in any way subject to its control and not members of the nucleus shall have the right to deliberate and vote with it concerning the work of their respective committees and shall be to such extent members of the Supervisory Committee.

- 3. The nucleus of five members may exercise the right to appoint, subject to its sole jurisdiction sub-committees to deal with methods of analysis that do not fall within the province of existing committees of the Society or of its Divisions or Sections.
- 4. All committees of the Society and of its Divisions and Sections, as well as sub-committees of the Supervisory Committee that are charged with recommending standard methods of analysis, shall submit their final reports to the Supervisory Committee for consideration.
  - 5. The Supervisory Committee shall:
    - (a) Exercise control of the work of all subordinate committees to the extent of preventing duplication of work and insuring consistency in the form of publication of reports.
    - (b) Examine all reports submitted to it that are final in the sense of definitely recommending methods or parts of methods for general use. This involves the right to reject entirely

such reports or to return them to the committee from which they emanate for such revision as may seem called for. It is assumed that no unduly arbitrary action will be taken in either of these directions, but that any decision rendered will be with a view to uphold the reputation of American chemists and the dignity of the Society. Any member of the Supervisory Committee may seek advice from experts of his own choice, regarding a report submitted to the committee.

- 6. Divisional or Sectional committees charged with recommending methods of analysis shall have full power, under the control of their respective Divisions or Sections, to initiate and prosecute work, and to publish, without referring to the Supervisory Committee, reports of progress and methods that are offered as tentative only. Final reports, however, or such as definitely recommend methods or parts of methods for general use shall be submitted by the chairman of the recommending committee to the Supervisory Committee for special consideration. Only on approval by that committee, except as hereinafter provided for, may such reports be published, subject to the usual submission to the editor of one or another of the Society's publications.
- 7. If the Supervisory Committee fails within three months to approve or reject a report submitted to it, the President of the Society (acting with the advice of the editors-in-chief of the Society's publications and of the chairman of the Division or Section concerned) shall be the final judge of its disposition. Similar disposition shall be made of reports that receive a tie vote in the Supervisory Committee. Acceptance or rejection within the time limit by the Supervisory Committee shall be final.
- 8. Final reports, if published, shall appear as emanating from the particular Division, Section, or sub-committee concerned, with the approval attached of the Supervisory Committee (or of the President of the Society in lieu of approval by the Supervisory Committee as called for in the foregoing rule 7) and they shall be signed by or appear under the names of a majority of the committee which prepared them, accompanied by a statement of the vote by which adopted.
- 9. Divisions or Sections of the Society may in their judgment appoint other general committees vested with power to appoint and control sub-committees within the Division or Section (referred to hereinafter as committees of first rank) or separate coördinate committees for different kinds of analytical work, but in the former case only the chairman of the committee of first rank shall have the restricted membership in the Supervisory Committee set forth in rule 2, paragraph 2.
- 10. The chairmen of all divisional or sectional committees of first rank shall, before a given line of work is undertaken, notify the chairman of the Supervisory Committee of the character and scope of the contemplated work, in order that duplication by different Divisions and Sections may be avoided. In case of impending duplication and subsequent inability of the Divisions or Sections interested to come to an agreement, the matter shall be decided by the Supervisory Committee.
- 11. In order to aid the chairman of the Supervisory Committee in the preparation of his annual report to the Council, the chairman of all divisional, sectional, and special committees shall each year submit to the Supervisory Committee a brief report of work in progress or about to be undertaken in their respective committees.

Said chairmen shall further report to the chairman of the Supervisory Committee at the earliest possible moment the correct names of their committees and sub-committees with a list of their members, and shall notify him of all changes made.

- 12. Joint committees of the Society with other societies shall report to the Supervisory Committee in the same way as prescribed in rules 6, 10, and 11, and the senior member by appointment from the American Chemical Society shall have the same rights and privileges in the Supervisory Committee as a chairman of a divisional or sectional committee.
- 13. The Supervisory Committee shall not approve any method of analysis which has been approved or adopted by another organization unless the method has been given a thorough and independent trial by a duly constituted committee within the American Chemical Society.
- 14. In order that Rules 1–13 may be brought promptly to the attention of all committees whose reports are subject to approval by the Supervisory Committee, the Secretary of the Society shall send copies of them to all newly elected Secretaries of Divisions and Sections accompanied by a request that they be transmitted to the chairmen of all committees on methods of analysis of their respective Divisions or Sections. The Secretary of the Society shall also send copies of the rules to the chairmen of newly appointed general committees of the Society that are charged with the formulation of standard methods of analysis.

All previous resolutions conflicting in part or wholly with the foregoing rules are hereby repealed. In promulgating the foregoing rules the Council wishes it understood that the Society does not contemplate making the use of such methods as may be recommended by its committees obligatory on any one, and, further, that no method is to be considered as final but simply as representing the best that can be done at the stated time. It is expected as a matter of course that revision will be exercised as knowledge and experience grow.

It was voted that new student memberships may begin on September 1st instead of on January 1st, in which case the dues will be \$3.50 for the last third of the year. Jour-

nals will be sent from September 1st, provided that back journals from that date are available.

A. B. Lamb was reëlected Editor of the Journal of the American Chemical Society, H. E. Howe, Editor of Industrial and Engineering Chemistry, W. A. Noyes, Editor of Scientific Monographs, and H. E. Howe, Editor of Technologic Monographs.

The following by-laws were passed:

Add to By-Law 3 the following two paragraphs:

There shall be an Executive Committee of the Council consisting of the immediate Past-President, the President, the Secretary, the Treasurer, the Editor of the Journal of the American Chemical Society, the Editor of Industrial and Engineering Chemistry, the Editor of Chemical Abstracts, and three Councilors, one to be elected each year for a term of three years, by ballot, at the annual meeting. A Councilor so elected shall remain a Councilor during his term of office on the committee.

The Executive Committee so constituted shall have full authority to act ad interim for and on behalf of the Council in all matters of national policy or import, shall serve in an advisory capacity in connection with matters coming before the Council, and shall exercise in addition the usual functions of an Executive Committee,

#### BY-LAW 22

The Directors shall be elected from districts arranged as nearly as possible to obtain equitable representation. At the time of election the Director shall reside or be a member of a section within the geographical limits of his district but shall not lose office by removal therefrom. Each local section, or any group of twenty-five members in good standing, within the district shall have the privilege of nominating one Director every three years, or whenever a vacancy occurs in their representation. For this purpose six districts are created as follows:

1st District. Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut and Canada.

2nd District. New York and New Jersey.

3rd District. Pennsylvania, Delaware, and Ohio.

4th District, Ålabama, Arkansas, District of Columbia, Florida, Georgia, Kentucky, Louisiana, Maryland, Mississippi, North Carolina, Oklahoma, South Carolina, Tennessee, Texas, Virginia, and West Virginia.

5th District. Illinois, Indiana, Michigan, and Wisconsin.

6th District. Alaska, Arizona, California, Colorado, Hawaii, Idaho, Iowa, Kansas, Minnesota, Missouri, Montana, Nebraska, Nevada, New Mexico, North Dakota, Oregon, South Dakota, Utah, Washington, and Wyoming.

Necessary traveling and hotel expenses of Directors incurred in attending meetings of the board, other than those held at the time of general meetings, shall be paid by the Society.

The following changes in the Constitution being duly signed by five members of the Council, were recommended to the membership for passage:

Change Article IV, Section 4, Paragraph 8, of the Constitution now reading as follows:

In like manner, on or before November I, the Secretary shall mail to each member of the Council a blank upon which the Councilor shall be entitled to express his choice for two directors. From the nominations so received, the Secretary shall mail to the Council the names of the four persons who shall have been certified as having received the greatest number of nominating ballots for the office of director, and the Council shall elect two directors from these candidates, by mail ballot, at least one week before the end of the year.

to read:

On or before October 1 of each year the Secretary shall request each local section (entitled as provided in By-Law 22) to nominate a candidate for director, which nomination shall reach him on or before November 20 to be valid. The Secretary shall mail to the Council the names of the nominees so received and the Council shall elect one Director from each of two districts from among these candidates, by mail ballot, at least one week before the end of the year.

Add to Article IV, Section 5 (c) of the Constitution the provision:

If reflected, an Editor shall be elected by the Council to serve a term of three years, beginning with the first day of January, or until his successor shall have been duly chosen.

It was voted that the names of the two Councilors already on the Advisory Committee be continued on the Executive Committee. George D. Rosengarten was then elected the third member of this Committee.

It was voted that the Advisory Committee be given a vote of thanks in recognition of their excellent work in connection with changes in the by-laws brought about through the recommendation of the Committee on Society Procedure.

It was voted that it is the sense of the Council that the Council is not too large as at present organized.

It was voted that the name of the Leather Division be changed to "Division of Leather and Gelatin Chemistry."

It was voted to lay upon the table the motion of the Chairman and Secretary of the Leather Division permitting the presentation of papers by non-members at the option of the chairmen and secretaries of Divisions, with the suggestion that this matter be considered by the group of divisional officers. It was later voted to amend the vote passed at Pittsburgh regarding papers by non-members, so that it shall read as follows:

Papers by non-members may be placed on the program only when of unusual importance, and then only with the joint approval of the Secretary of the Division and the Secretary of the Society, except papers invited by chairmen and secretaries of Divisions, and such papers shall be so designated on the program.

It was voted that the Council approve the action of the Secretary so far taken in limiting papers of non-members and instruct him to continue the present policy of the Council, except as provided in the preceding motion.

The following resolution was presented by Professor E. C. Bingham, Chairman of the Metric System Committee, and was adopted:

In view of the earnest effort of the scientific, medical, pharmaceutical, and engineering societies of America in favor of the gradual adoption of the metric system, the Council of the American Chemical Society regrets the action of the U. S. Public Health Service and the War Department in making specifications for reagent chemicals hereafter in avoirdupois and apothecary units.

It was voted that the officers of the Society be complimented upon having accomplished so wide a distribution of our conferences.

It was voted that the Council encourage the holding of intersectional meetings with Section C of the American Association for the Advancement of Science.

The Council then discussed for some two hours the question of intersectional meetings and classified membership without action.

A vote of thanks was passed to those in Milwaukee who had made the meeting so successful.

The Council then adjourned.

CHARLES L. PARSONS, Secretary

## MEMBERS ELECTED BETWEEN JULY 15, 1923 AND SEPTEMBER 15, 1923 Atkins, Thomas J., D. S. P. House, University, Va. Aubey, Arnold B., 415 North Park St., Madison, Wis. Bain, M. J., R. R. No. 4, Box 118, Martinsville, Indiana. Ball, Samuel Graham, Box 159, Dunlop Rubber Co., Far East, Ltd., Kobe, Japan. Becker, Herbert W., 1056 45th St., Milwaukee, Wis. Bishop, Alfred E., 180 S. College St., Akron, Ohio. Blake, Kenneth Bradley, 178 Rast Center St., South Manchester, Conn. Boos, C. M., 114 N. Locust St., Aurora, Ill. Brandow, Walter M., Colgate University, Hamilton, N. Y. Burchenal, C. D., Allied Chemical & Dye Corp., 61 Broadway, New York City. Byrd, George, 560 Milwaukee St., Milwaukee, Wis. Campbell, John, Abitibi Power & Paper Co., Iroquois Falls, Northern Ont., Canada. Craig, Dudley Peak, 613 Harvey Ave., West Lafayette, Ind. Cuthbert, F. T., Solar Refining Co., Lima, Ohio. Drake, Lewis Marvin, West Fairview Ave., Daytona, Florida. Ehler, Otto, 2833A North 20th St., St. Louis, Mo. Fancher, George H., 714 S. Crawford St., Downey, Cal. Fitz, Leslie Arthur, 158th St., and Mott Ave., New York City. Gerhardt, Fisk, Agri. Expt. Station, Chemistry Section, Ames, Iowa.

Gibbons, Willis A., 561 W. 58th St., New York City.

Golding, Charles D. Douglas, Natal Technical College, Durban, Natal, South Africa,

Haglund, George, Ljusne, Sweden.

Hale, Worth, 240 Longwood Ave., Boston, 17, Mass.

Higgs, Roy E., 811 Woodlawn Ave., Buffalo, N. Y.

Hilger, Sister Marie, St. Benedict's College, St. Joseph, Minn.

Irby, William, Y. M. C. A., Lynn, Mass.

Keats, John L., 1100 N. Adams St., Wilmington, Del.

Klaiber, Walter J., 129 N. Menard Ave., Chicago, Ill.

Koenig, Hedwig A., 585 E. 178th St., New York City.

Kraus, Charles A., Clark University, 950 Main St., Worcester, Mass.

Lange, Edward John, Box 236, San Pedro, Cal.

Laudig, John F., 613 Pressley St., N. S., Pittsburgh, Pa.

Leopold, Geneva, 169 Alden Ave., New Haven, Conn.

Lindstrand, Uno, 1531 Front St., Sacramento, Cal.

Merion, Howard D., Ward, Pa.

Merrill, Alice Thompson, Hygienic Lab., 25th & E Sts., N. W., Washington, D. C.

Mona, George, 63 Foundry St., Central Falls, Rhode Island.

Morison, Clifford Brewster, 1135 Fullerton Ave., Chicago, Ill.

Nevers, Ralph P., 12 School St., Salem, Mass.

Norton, Marian J., 1 Summit St., Whitinsville, Mass.

Olsen, Aksel G., Postum Cereal Co., Battle Creek, Mich.

Paniker, Ramon, Apartado 797, Barcelona, Spain.

Powell, Charles Wilfrid Roberts, Colonial Sugar Refining Co., Ltd., Sydney, N. S. W., Australia.

Price, Charles W., Box 222, Sweetwater, Tenn.

Rask, Olaf Selmer, School of Hygiene and Public Health, Johns Hopkins Univ., Baltimore, Md.

Rider, Arthur J., 400 Oak Ave., Ithiaca, N. Y.

Rincliffe, Roy George, 114 E Madison St., Sandusky, Ohio.

Ritchie, Kenneth S., Box L180, Stanford University, Cal.

Roessinger, Walter C., 37 Greenpoint Ave., Brooklyn, N. Y.

Roberts, E. D., Hawaiian Sugar Co., Makaweli, Kauai, T. H.

Schulz, Ernest R., 803 State St., Madison, Wis.

Sewell, Earl A., Hendry Apts., Angola, Indiana.

Shear, Murray J., 625 Bedford Ave., Brooklyn, N. Y.

Simon, Raub H., Ohio Agri. Expt. Station, Wooster, Ohio.

Sloan, Howard Backus, 179 Redington St., Swampscott, Mass.

Sloan, Tom K., Box 478, Route I, Mountain View, Cal.

Smith, Edward H., 564 W. 160th St., Apt. 64, New York City. Steinour, Harold H., P. O. Box 427, Lompoc, Cal.

Stephens, Ruth, 1880 Lincoln Ave., St. Paul, Minn.

Strimbeck, George Richard, Jr., 122 S. Porter St., Saginaw, W. S., Michigan.

Thomas, Geo. C., 3811/2 Kenwood Blvd., Milwaukee, Wis.

Tucker, Elton B., Hershey, Pa.

Turull, William C., 140 Liberty St., New York City.

Whiting, L. R., 5615 Prairie Ave., Chicago, III.

Williams, Alexander, Jr., 81 Fulton St., New York City.

Wyld, Wilfrid, care of Post Office, Street Lane, Roundhay, Leeds, England.

#### CORPORATION MEMBERS

Bird & Son, Inc., East Walpole, Mass.

Duram, Limited, Duram Works, near Church Road, Hanwell, London, W. England.

J. R. Geigy, S. A., Basle, Switzerland.

The Palmolive Company, 4th & Fowler Sts., Milwaukee, Wis.

#### DECEASED

Harry M. Gordin, 31 W. Lake St., Chicago, Ill. Died, July 5, 1923.

Robert W. Hilton, 432 New St., Cincinnati, Ohio. Died, February 5, 1923.

Parker C. McIlhiney, 52 E. 41st St., New York City. Died, June 21, 1923.

Arthur E. Rice, 1010 Widener Bldg., Philadelphia, Pa. Died, Aug. 26, 1923.

F. C. Rose, 61 Broadway, New York City. Died, June 22, 1923.

Clarence M. Sherwood, Hercules Powder Co., Brunswick, Ga. Died, Mar. 5, 1923.

Stephen P. Sharples, 22 Concord Ave., Cambridge, Mass. Died, Aug. 20, 1923.

# Proceedings

# COUNCIL

MEMBERS ELECTED BETWEEN SEPTEMBER 15 AND OCTOBER 15, 1923

Allen, Homer G., 29 W. Girard Blvd., Kenmore, N. Y. Bardin, Collis M., 702 E. Buffalo St., Ithaca, N. Y. Beck, D. B., 175 Littleton St., West Lafayette, Ind. Berry, Walter M., 806 Pacific Finance Building, Los Angeles, Cal. Blackwell, Ashby C., Morris Harvey College, Barboursville. W. Va. Coulson, Donald C., 565 West Washington, Chicago, Ill. Crone, E. B., Sandoval, Illinois. Crum, F. B., 1106 W. Main, Urbana, Ill. Dougherty, Frank, 12106 Mt. Overlook Ave., Cleveland, Ohio. Erwin, James H., 315 University St., West Lafayette, Ind. Grote, Irvine W., 217 Poplar St., Chattanooga, Tenn. Gruenerwald, Carl A., 315 Winter St., Pekin, Ill. Gustavson, Karl Helmer, Widen-Lord Tanning Co., Danvers, Mass, Herbst, Julius, 315 E. 166th St., New York City. Hopkinson, Ernest, 1790 Broadway, New York City. Horton, Ralph E., Huntington, L. I., N. Y. Hosterman, Ralph Cook, 1109 South St., Lafayette, Ind. Kida, Yuji, Chem. Lab., College of Science, Imperial University, Kyoto, Japan. Kimura, Sakujiro, Chemical Laboratory, College of Science, Imperial University, Kyoto, Japan. Lopin, Miss Anna Mildred, Box 52, Orland P. O., Cal. Malatesta, Andrew B., Dept. of Agronomy, Texas Agri. Expt. Sta., College Station, Texas. Money, Harold N., 1116 Harrison St., Davenport, Iowa. Moul, Horace C., 41 Carisle St., Hanover, Pa. Pierson, Gordon G., Perkins Glue Co., Lansdale, Pa. Pitzer, John C., 518 W. Maumee St., Angola, Indiana. Rape, Edwin H., Swift & Co., Fertilizer Works, Atlanta, Ga. Rieman, Wm. 3rd, Rutgers College, Chemistry Department, New Brunswick, N. J. Sawyer, Roscoe H., Matthews 20, Cambridge, Mass. Simonds, Paul W., 428 Transportation Building, Chicago, Ill. Weatherwax, James L., 932 N. 65th St., Philadelphia, Pa. Welti, Erich R., 15 Bellevuestrasse, Berne, Switzerland. Wenning, Wm. F., 3354 Francisco St., Corliss Station, Pittsburgh, Pa. Wilhelm, R. Mason, 88 33rd St., % C. J. Togliabua Mfg. Co., Brooklyn, N. Y. Wood, Frank J., 153 Joralemon St., Brooklyn, N. Y.

# MEETINGS OF THE SECTIONS

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

#### ALABAMA SECTION

The regular monthly meeting of the Section occurred on October 6, at the Hillman Hotel, Birmingham, Alabama. The following program was presented: "Purification of Benzol," by S. S. Heide; "Quality of Coke in Reference to Blast Furnace," by W. H. Oldham; and "Electrolytic Manufacture of Phosphorus Products," by Theo. Swann.

HARRY BURN, Secretary

#### AMES SECTION

On June 12, W. Lash Miller, of the University of Toronto, gave a short illustrated talk before the members of the Section, his subject being "The Development of Alchemy."

R. B. WAITE, Secretary

#### CALIFORNIA SECTION

The 141st regular meeting of the Section was held on September 7, at the Engineers' Club, San Francisco, Cal. The following program was presented: "The Synthesis of Ammonia from Its Elements," by A. R. Olson; and "Peculiarities in Reactions of Unsaturated Carbon Compounds," by T. D. Stewart, both of the University of California.

L. H. Duschak, Secretary

#### CHICAGO SECTION

The regular meeting of the Section was held on September 21, at the City Club, Chicago. The address of the evening was by Carl S. Miner, of The Miner Laboratories, Chicago, Ill., his subject being "Furfural—The Story of an Industrial Research." The usual group meetings were held.

On October 19, A. M. Buswell, chief of the Illinois State Water Survey, addressed the members of the Section, his subject being "Sewage Purification: A Chemical Manufacturing Process."

Lee F. Supple, Secretary

#### DETROIT SECTION

At a joint meeting of the Associated Technical Societies of Detroit, held on October 26 under the auspices of the Local Section of the American Chemical Society, Edwin E. Slosson, of Washington, D. C., spoke on "Economic Independence of the United States."

J. D. PATERSON, Secretary

#### INDIANA SECTION

On October 12, W. D. Harkins, of the University of Chicago, addressed the meeting of the Section, his subject being "The Reality of the Atom. Photograph of Atom Tracks and Atomic Collisions."

H. A. Showle, Secretary

#### IOWA SECTION

The first meeting of the season was held on October 17, when the following program was presented: "A Report on the Milwaukee Meeting," by Edward Bartow; "The Influence of Gum Arabic upon the Catalysis of Methyl Acetate," by J. N. Pearce; and "A Report on Progress in the Determination of Solubilities," by P. A. Bond.

G. H. COLEMAN, Secretary

# KANSAS CITY SECTION

On September 21, the local Section joined with the University of Kansas and the Kansas Academy of Science in a celebration in honor of Edgar Henry Summerfield Bailey upon the completion of his fortieth year of service as professor of chemistry at the University of Kansas.

L. E. Clark, Secretary

# LEHIGH VALLEY SECTION

On September 28, the Section was addressed by Newton Perrins, of the Eastman Kodak Co., who spoke on "Curious Patents."

On October 26, James Kendall, of Columbia University, spoke to the members of the Section, his subject being "Isotopes." R. H. Bogub, Secretary

# LEXINGTON SECTION

The 89th meeting of the Section was held on October 4, at the University of Kentucky, Lexington, Ky. A report on the annual meeting of the Society at Milwaukee was made by J. S. McHargue.

O. M. Shedd, Secretary

#### LOUISVILLE SECTION

On September 19, the local Section held a meeting to discuss plans for the year's meetings and interesting new members in the Society.

C. E. Geiger, Secretary

#### NEBRASKA SECTION

At the 110th meeting of the Section held on September 18, E. C. Franklin, president of the American Chemical Society, spoke on "The Ammonia System of Acids, Bases and Salts."

S. B. Arenson, Secretary

#### NEW HAVEN SECTION

The first fall meeting of the Section occurred on October 17, when James W. Mc-Bain, of the University of Bristol, spoke on "A Study of Soap Solutions and its Bearing Upon Colloid Chemistry."

BLAIR SAXTON, Secretary

#### NEW YORK SECTION

At the meeting of the Section, held on October 5, the following program was presented: "Vitamins as Factors in Food Values," by Henry C. Sherman, of Columbia University; "The Manufacture and Uses of Invert Sugar," by Stroud Jordan, of the Henry Heide Company; "Some Salient Points in Sugar Manufacture and Economics," by David L. Davoll, of Arbuckle Brothers; and "Bread and its Relation to our Diet," by F. C. Weber, of the Fleischmann Laboratory.

Benjamin T. Brooks, Secretary

#### NORTHEASTERN SECTION

The 187th meeting of the Section occurred on October 15, when James W. McBain, of the University of Bristol, spoke upon "A Study of Soap Solutions and its bearing Upon Colloid Chemistry."

E. B. Millard, Secretary

#### OMAHA SECTION

The regular meeting of the Section was held on September 4, at Creighton University, Omaha, Nebraska. The following papers were given: "A Biography of Dalton," by Rev. Father Hickey, and "Milk Born Infection (Illustrated)," by R. N. Perkins.

The meeting of the Section, held on October 5, was addressed by A. H. Sabin, on the subject of "Paints."

R. N. Perkins, Secretary

# PITTSBURGH SECTION

The regular meeting of the Section occurred on September 20. A written report by James O. Handy, on the Milwaukee meeting, was read. It was voted that the Pittsburgh Section grant waivers on Blair County to the newly formed central Pennsylvania Section. Several business matters were considered by the meeting.

On October 18, Richard Bishop Moore, of the Dorr Company, New York City, addressed the members of the Section, his subject being "Newly Discovered and Undiscovered Elements."

E. S. Stateler, Secretary

#### ROCHESTER SECTION

On September 29, the Rochester and Syracuse Sections held a joint outing at the Geneva Experiment Station. In addition to the various amusements presented, an illustrated lecture was given by D. D. Van Slyke, of the Rockefeller Institute, his subject being "Factors Controlling the Distribution of Water and Electrolytes in the Blood."

ERLE M. BILLINGS, Secretary

# SAINT LOUIS SECTION

At the meeting of the Section, held on October 1, O. S. Ledman, of the Luyties Pharmacy Company, gave a paper on "The Homeopathic Laboratory." Reports on the Milwaukee meeting by the local councilors were made.

H. A. Carlton, Secretary

#### SOUTHERN CALIFORNIA SECTION

On July 26, W. Lash Miller, of Toronto, Canada, spoke before the meeting of the Section, his subject being "The Method of Willard Gibbs in Chemical Thermo-Dynamics."

At a joint session by the Southern California and California Sections, held on September 19, the following program was presented: "New Studies in Nitrogen Fixation," by C. B. Lipman; "Present Status of Chemical Criteria in Soil Fertility Investigations," by John Burd; "The Determination of Calcium," by Wm. Conger Morgan; "Critical Solution Temperatures," by G. Ross Robertson; "A Study of Pressure and Temperature Effects on Petroleum Emulsions," by Laird J. Stabler; "Butyrin," by Leroy S. Weatherby; "The Vapor Pressure of Monatomic Elements," by Russell H. Miller; "A System of Qualitative Analysis Including the Rare Elements," by A. A. Noyes and W. C. Bray; "Dissociation of Hydrogen Cyanide at High Temperatures," by R. M. Badger; "The Rate of Dissociation of Sulphuryl Chloride," by D. F. Smith; "Studies on the Chemical Behaviour and the Physical Properties of Insulin," by G. A. Alles and A. L. Raymond; "Some New Experiments on the Oxidation Reduction Theory of Contact Catalysis," by A. F. Benton and P. H. Emmett.

On October 12, Gustave Egloff, of the Universal Oil Products Co., of Chicago, spoke on "The Refining of Petroleum Oil."

MARK WALKER, Secretary

#### UNIVERSITY OF ILLINOIS SECTION

At the regular monthly meeting of the Section, held on October 16, R. E. Greenfield, of the Illinois State Water Survey, spoke on "Investigation of Pollution of the Illinois River."

D. T. ENGLIS, Secretary

#### UNIVERSITY OF MISSOURI SECTION

The 117th meeting of the Section was held on September 20, when P. A. Shaffer, of Washington University, St. Louis, Mo., spoke on "The Preparation and Properties of Insulin."

H. E. French. Secretary

#### VIRGINIA SECTION

On October 12, E. R. Weidlein, director of the Mellon Institute, Pittsburgh, Pa., addressed the Section on "Science and Industry."

On October 18, 19 and 20, Edwin E. Slosson, at the invitation of the Section and the University of Virginia, spoke on the following subjects, respectively: "Creative Chemistry," "The Changing Mind of Man," and "Science Remaking Everyday Life."

LLOYD C. BIRD, Secretary

#### WISCONSIN SECTION

The 127th regular meeting of the Section occurred on October 10, when H. B. Wahlin, of the University of Wisconsin, spoke on "The Nature of Gaseous Ionization."

FARRINGTON DANIELS, Secretary

#### WASHINGTON, D. C., SECTION

The 344th regular meeting of the Section was held on October 11. The address of the evening was by E. W. Washburn, of the National Research Council, who spoke on "Physical Chemistry and Ceramics."

J. B. Reed, Secretary

# WESTERN NEW YORK SECTION

At the meeting of the Section, held on October 16, a general discussion of the following subjects was carried on: "Were You Properly Educated?" "Are Future Chemists Being Properly Educated?" and "Why is Chemistry Being Taught as It Is?"

R. W. HESS, Secretary

#### DECEASED

Pierre Mali, 25 Madison Ave., New York, N. Y. Died, October 4, 1923.

Benjamin S. Neuhausen, 2213 Madison Ave., Baltimore, Md. Died, August 20, 1923.

Frank D. Simons, U. S. Appraiser's Public Store Building, Baltimore, Md. Died, October 5, 1923.

# Proceedings

# COUNCIL

Dr. E. C. Franklin, President of the American Chemical Society, appointed Edward Mallinkrodt to represent the Society at the inauguration of Herbert Spencer Hadley as chancellor of Washington University, St. Louis, Mo. Dr. Franklin also appointed W. F. Hillebrand to represent the Society at the inauguration of William Mather Lewis as president of George Washington University, Washington, D. C.

# MEMBERS ELECTED BETWEEN OCTOBER 15 AND NOVEMBER 15, 1923

Baker, Thaddeus H., 7212 Ridgeland Ave., Chicago, Ill.

Bakken, A. C. Aluminum Club, New Kensington, Pa.

Baril, Olier L., 1 Cottage St., Spencer, Mass.

Barrell, Edward Park, 430 East Rich Ave., De Land, Fla.

Beebe, Ralph A., Gateway Club, Princeton, N. J.

Binswanger, L. Clarence, 829 North 3rd St., Philadelphia, Pa.

Blatchford, Rev. John A., Holy Cross College, Worcester, Mass.

Bloomsburg, Harry E., 1004 Furnald Hall, Columbia University, New York City,

Bodman, J. W., Room 701, 360 N. Michigan Blvd., Chicago, Ill.

Bosonitz, John J., 211 University St., W. Lafayette, Ind.

Branham, Joseph Russell, Cobb Chem. Lab., University of Virginia, University, Va.

Brubaker, Merlin, 1104 West Clark St., Urbana, Ill.

Bull, H. Marie, Albion College, Library, Albion, Mich.

Burns, A. L., 225 Custom House, New Orleans, La.

Burroughs, A. M., 12 Whitten Hall, University of Missouri, Columbia, Mo.

Caeser, David, 1501 Eastern Parkway, Brooklyn, N. Y.

Case, Jarvis Dixon, 23 Harvard St., Hartford, Conn.

Chittum, John W., 5517 Dorchester Ave., Chicago, III.

Coe, Dana G., Soils Department, Iowa State College, Ames, Iowa.

Davidson, Glen M., 515 W. 111th St., New York City.

de Ganahl, Carl, Medway Oil Storage & Refg. Co., Grain Halt, Isle of Grain, Kent, England.

de Goey, Cornelius, American Wringer Co., Woonsocket, R. I.

Donaldson, David, 60 Polwarth Terrace, Edinburgh, Scotland.

Drake, Richard C., 602 E. Stoughton, Champaign, Ill.

Dumit, Michael J., Brown Corporation, La Tuque, Que., Canada.

Evans, R. M., Fixed Nitrogen Research Lab., Washington, D. C.

Evans, Thomas R., 1452 Beechwood Blvd., Pittsburgh, Pa.

Fernow, Wilson C., Aluminum Club, New Kensington, Pa.

Fisk, Henry G., 1105 Nevada, Urbana, Ill.

Fluhrer, Earle R., Box 261, Iowa City, Iowa.

French, C. Clement, 5127 N. 16th St., Philadelphia, Pa.

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Gilchrist, Peter S., 1206 S. Boulevard Charlotte, N. C.

Gray, F. Anton, School of Chemistry, University of Minnesota, Minneapolis, Minn.

Gray, M. P., 608 Garfield Ave., Valparaiso, Indiana.

Green, Alfred H., 2024 Broadway, Indianapolis, Ind.

Greenberg, David Morris, Biochemistry Dept., University of California, Berkeley, Cal.

Guest, Arthur E., Chemistry Building, Iowa State College, Ames, Ia.

Guyer, J. A., 15 Belden Ave., La Salle, N. Y.

Hager, F. D., 209 Chemistry Bldg., Urbana, Ill.

Hammond, John A., P. O. Box 71, Stege, Cal.

Hanaway, W. L., Custom House, Savannah, Ga.

Harkness, Roy W., 1011 W. Springfield Ave., Urbana, Ill.

Harris, Carl A., c/o A. S. Bolling, Preston Heights, University, Va.

Hatman, Julius G., Valley Road, Oak Lane Station, Philadelphia, Pa.

Hauge, Sigfred M., Agricultural Experiment Station, Purdue University, LaFayette, Ind.

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Hawes, Charles C., 709 North Main St., Ishpeming, Mich.
Hines, Paul R., Ridge Road and Buckingham Drive, Cleveland, Ohio.
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Jebb, William Thomas, 518 Hamilton St., Allentown, Pa.
Johnson, Charlton Frost, Berkshire School, Sheffield, Mass.
Johnson, Wm. H., 314 South Clinton St., Iowa City, Iowa.
Joshi, Anant Keshav, 611 W. Elm, Urbana, Ill.
Kaffke, Caspar, 673 Northampton St., Easton, Pa.
Keohan, William F., 1843 S St., Washington, D. C.
Kinney, Ethyl May, Western College for Women, Oxford, Ohio.
Koenig, Ernst, Farbwerke vorm Meister Lucius & Bruning, Hoechst on Main, Germany,
Kragle, Darwin P., 292 Pine St., Freeport, L. I., N. Y.
Kuehramann, O. W., 519 Waldron St., W. Lafayette, Ind.
Lake, William W., 1422 North State Parkway, Chicago, Ill.
Landis, Quick, 3289 Montana St., Oakland, Cal.
Lincoln, Emery W., Box 158, North Dighton, Mass.
Lurie, Daniel, Furnald Hall, Columbia Univ., New York City.
Mackie, Robert F., 23 St. Botolph St., Boston, Mass.
Martin, Frank D., 220 Waldron St., W. Lafayette, Ind.
Matheson, G. Lawrence, 69 Russell Ave., Ottawa, Canada.
McClure, Frank James, 202 North St., W. Lafayette, Ind.
McCoy, John T., 35 Lee St., Cambridge, Mass.
Mertz, R. Fay, 217 Harrison St., W. Lafayette, Ind.
Milner, Reid T., 502 E. John St., Champaign, Ill.
Minton, P. E., Acme-Evans Co., Indianapolis, Ind.
Mleynek, F. J., 4025 Izard St., Omaha, Neb.
Moore, Milton J., 1633 Sierra Bonita Ave., Los Angeles, Cal.
Moy, J. Hymn, 886 Washington St., San Francisco, Cal.
Nixon, Glenn C., 2854 West St., Ames, Iowa.
Parsons, Charles E., 149 Church St., New York City.
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Peter, Richard C., 519 Stewart Ave., Ithaca, N. Y.
Peterson, J. M., 207 S. Hyland Ave., Ames, Iowa.
Powers, J. L., 914 Hill St., Ann Arbor, Mich.
Preston, Walter C., 747 Beechwood Ave., Winton Place, Cincinnati Ohic
Rankin, Gray S., 340 E. First St., Albany, Oregon.
Rapp, Paul, 1736 G St., N. W., Washington, D. C.
Rippie, Charles W., 602 West Nevada St., Urbana, Ill.
Roberts, C. H. M., 937 Pacific Ave., Webster Groves, Mo.
Rufe, Redding H., Alpha Zeta Frat., State College, Pa.
Ruggli, Eva M., 399 Broadway, Cambridge, 39, Mass.
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Schaler, Charlotte M., 1311 Austin St., Houston, Texas.
Scherer, Philip C., Jr., 2 Charles Field Court, Providence, R. I.
Schueman, W. W., Aluminum Club, New Kensington, Pa.
Schupp, O. E., Jr., Box 255, University Station, Tucson, Ariz.
Scott, Jasper P., 432 West 31st St., Indianapolis, Ind.
Shepard, Harry L., 218 Grace St., Council Bluffs, Iowa.
Shive, Roy A., State Water Survey, Chemistry Building, University of Illinois, Urbana, Ill.
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Smith, S. Reagan, Ga. Experiment Station, Experiment, Ga.
Standish, Clara M., Talladega College, Talladega, Ala.
Stern, Louis, 1817 Mohegan Ave., New York City.
Strickhouser, Sherman I., 57 Chemistry Bldg., Urbana, Ill.
Sy-Quai, Pedro M., 123 Quarry St., Ithaca, N. Y.
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Wilson, Wright W., 224 W. Michigan Ave., East Lansing, Mich.
Winston, Dr. J. H. C., Hampden-Sidney College, Hampden-Sidney, Va.
Wright, Wilsorn H., Syra-Cord Tire & Rubber Co., East Syracuse, N. Y.
Yamada, Sakura, 51 Aoyama Minami-machi 5-Chome, Akasaka-ku, Tokyo, Japan.
Yeatts, Howard S., 522 Ridge St., Charlottesville, Va.
Zitzmann, Karl N., Ajax Rubber Co., Racine, Wis.

# MEETINGS OF THE SECTIONS

(Full accounts of all meetings should be sent to Secretary Charles L. Parsons, 1709 G St., N. W., Washington, D. C.)

#### AMES SECTION

On the evening of October 25, A. M. Buswell, chief of the Illinois State Water Survey, addressed the Section. His subject was "Sewage Purification, a Chemical Manufacturing Process."

R. B. Waite, Secretary

#### ARKANSAS SECTION

The fall meeting of the Section was held at Little Rock, Arkansas, on November 8, 1923. The following program was presented: "Diamonds Set in Platinum," by Frank W. Gibb; "Recent Advances in our Understanding of Insecticides," by George Becker; "Industrial Alcohol," by Ruel J. Manning; "Origin of Arkansas Bauxite," by George Banner; and "Insulin and the Diabetic," by J. W. Read.

The following officers for 1923-1924 were elected by the Section: J. W. Johnson, chairman; G. W. Roark, Jr., vice chairman; Harrison Hale, councilor; H. G. Lewis, treasurer; and J. W. Read, secretary.

J. W. Read, Secretary

#### CALIFORNIA SECTION

The 142nd regular meeting of the Section occurred on October 12, when Jerome Alexander, of the National Research Council, Washington, D. C., spoke on "Bridging the Gap between Masses and Molecules."

The 143rd regular meeting of the Section was held on November 2, when the following addresses were given: "The Electrolytic Separation of Amino Acids," by C. L. A. Schmidt; and "The Chemistry of Humins," by G. O. Burr—both of the University of California.

L. H. Duschar, Secretary

#### CHICAGO SECTION

On November 23, Raymond F. Bacon, of the Standard Oil Company of Indiana, addressed the meeting of the Section, his subject being "Sulfur." The usual group meetings occurred after the lecture.

Lee F. Supple, Secretary

#### CINCINNATI SECTION

The first fall meeting of the Section was held on October 23, when James W. McBain, of the University of Bristol, Bristol, England, spoke on "A Study of Soap Solutions and Its Bearing Upon Colloid Chemistry."

The 261st regular meeting occurred on November 14, with the following program: "The Liberation of Hydrogen from Carbon Compounds," by H. S. Fry; and "The Composition of Marine Animal Oils," by C. L. Milligan—both of the University of Cincinnati.

A. O. SNODDY, Secretary

#### CLEVELAND SECTION

The first fall meeting of the Section was held on October 23, when Elbert L. Hyde addressed the members on the subject of "Patents."

H. S. BOOTH, Secretary

#### COLORADO SECTION

At the regular meeting of the Section, held on September 26, the following officers were elected: S. J. Osborn, chairman; L. D. Roberts, vice chairman; D. K. Proffitt, secretary; R. G. Gustavson, treasurer; and W. D. Engle, councilor.

D. K. PROFFITT, Secretary

#### COLUMBUS SECTION

On October 31, C. W. Foulk addressed the members of the Section, his subject being "Some Problems in the Industrial Use of Water."

Jesse E. Day, Secretary

## CONNECTICUT VALLEY SECTION

At the meeting of the Section, held on October 6, at Westfield, Mass., Dennis, Calhune, of the Worcester Polytechnic Institute, spoke on "Recent Developments in Electro-Chemistry."

On November 3, Arthur J. Hopkins, of Amherst College, addressed the members of the Section, at Hartford, Conn., his subject being "Traces of Alchemy." At this meeting, the following officers were elected for the Section: G. Albert Hill, chairman; George B. Hogaboom, vice chairman; E. W. Lovering, secretary; Henry McDonald, Jr., treasurer; C. R. Hoover and J. S. Chamberlain, councilors; H. Edward Wells, V. K. Krieble and J. A. Newlands, executive committee.

E. W. Lovering, Secretary

#### DELAWARE SECTION

The fall season of the Section was inaugurated on September 26, with an informal get-together dinner followed by an address by Graham Edgar of the University of Virginia. His subject was "Atomic Weights and Isotopes."

On October 18, W. M. Corse, of the National Research Council, Washington, D. C., addressed the members of the Section, his subject being "Nickel, Its Metallurgy and Uses."

At a meeting of the Section, held on November 21, Fred E. Wright, of the Geophysical Laboratory, Washington, D. C., addressed the members, his subject being "The Purpose and Scope of the Experiment in Geology."

J. W. Stillman, Secretary

#### EASTERN NEW YORK SECTION

At the regular meeting of the Section, held on November 2, Paul E. Howe, of the Rockefeller Institute of Medical Research, delivered a lecture on the subject, "Some Observations on the Globulins of the Blood."

On November 23, Karl T. Compton, of Princeton University, spoke on the subject, "The Distribution of Electric Charge and Mass in Molecules." H. A. Jones, Secretary

#### HAWAIIAN SECTION

The following officers for the Section were elected at its annual meeting held on October 24: Guy R. Stewart, chairman; William Weinrich, vice chairman; R. Q. Smith, secretary; D. Kirschman, treasurer; and Will T. McGeorge, councilor. At this meeting, F. F. Jewett, of Oberlin College, gave a short address on his experiences as a student and teacher.

Ronald Q. Smith, Secretary

#### INDIANA SECTION

The regular monthly meeting of the Section occurred on November 9, when A. B. Davis, of Cincinnati, Ohio, spoke to the members, his subject being "Advances in the Manufacture of Dry Colors and Their Application."

HORACE A. SHONLE, Secretary

# LEHIGH VALLEY SECTION

On November 22, Duff Abrams, of the Lewis Institute, Chicago, addressed the members of the Section, his subject being "Cements." ROBERT H. BOGUE, Secretary

# LEXINGTON SECTION

The 90th meeting of the Section was held on November 14. On that occasion, G. D. Buckner, of the Experiment Station, Lexington, Ky., spoke on the subject, "Scientific Meetings in France."

O. M. Shedd, Secretary

#### LOUISIANA SECTION

The first meeting of the season occurred on October 19, when S. A. Mahood, of of Tulane University, addressed the Section, his subject being "The Preparation of a New Dye—The Furfural Analog of Benzoflavine or Dimethyl-Furyl Acridine Hydrochloride."

On November 7, a dinner was given by members of the Section in honor of visiting members of the chemical fraternity—C. A. Browne, chief of U. S. Bureau of Chemistry, Washington, D. C., and R. E. Doolittle, chief of the central district, Bureau of Chemistry, U. S. Department of Agriculture.

H. R. Struens, Secretary

#### MAINE SECTION

A meeting of the Section was held on November 16, when H. E. Thompson spoke on "Application of Chemistry to Medicine."

L. G. Jenness, Secretary

#### MARYLAND SECTION

At the meeting of the Section, held on October 26, the following officers were elected for the ensuing year: Carl Haner, chairman; Neil E. Gordon, vice chairman; Adolph Harvitt, secretary-treasurer; A. A. Backhaus, A. E. Marshall and M. D. Scott, councilors; S. T. Powell, W. B. D. Penniman, J. C. W. Frazer, F. M. Boyles, W. A. Taylor and A. H. Warth, executive committee.

The Section held a joint meeting with the Baltimore Gas and Electric Association on November 21, when F. W. Speer, Jr., of the Koppers Company, spoke on "Liquid Purification of Illuminating Gas."

ADDLEH HARVITT, Secretary

#### MIDLAND SECTION

The 19th regular meeting of the Section occurred on October 19, when R. B. Moore, of the Dorr Engineering Company, New York City, gave an address on "Helium: Its History, Production, and Commercial Uses."

John A. Gann, Secretary

# MINNESOTA SECTION

On October 3, the Section heard reports on the Council meeting held at Milwaukee in September. Nominations for offices of the national society were made.

L. M. HENDERSON, Secretary

## NASHVILLE SECTION

The first fall meeting of the Section was held on October 26, and was addressed by J. W. Sample, state chemist of Tennessee, on the subject, "The Chemist in Regulatory Work."

H. A. Webb, Secretary

# NEBRASKA SECTION

The 111th meeting of the Section occurred on October 24, at the University of Nebraska, and was addressed by Charles W. Rodewald on "Synthetic Drugs: Some Theories of Physiological Action."

S. B. Arenson, Secretary

# NEW HAVEN SECTION

At the regular meeting of the Section, held on November 21, C. H. Davis, of the American Brass Co., spoke on "Spectroscope Analysis."

BLAIR SAXTON, Secretary

#### NEW YORK SECTION

Taking as his subject, "Bonds Between Atoms in Molecules," Lauder W. Jones, of Princeton University, addressed the meeting of the Section, November 9.

BENJAMIN T. BROOKS, Secretary

#### NORTHEASTERN SECTION

The 188th meeting of the Section was held on November 9, when the following addresses were given: "The Manufacture of Sodium Hydrosulfite," by L. A. Pratt, director of research, Merrimac Chemical Company; and "A Recent Improvement in Sulfuric Acid Manufacture," by F. G. Stantial, vice president of the Merrimac Chemical Co.

12. B. MILLARD, Secretary

#### NORTHERN INDIANA SECTION

The local Section held a joint meeting with the American Society for Steel Treating on October 24. The following addresses were made: "The Investigation of the Patigue of Metals," by Prof. Moore of the University of Illinois; and "The Relation Between the Experienced Employer and the Young Apprentice," by Walter F. Newhouse, of the Saranac Machinery Co.

At the regular meeting of the Section, held on November 14, W. D. Harkins, of the University of Chicago, spoke on "The Structure of the Atom."

V. C. BIDLACK, Steretury

#### NORTHERN WEST VIRGINIA SECTION

The first fall meeting of the Section occurred on October 19, when E. L. Rogers, of the Fairmont Normal School, Fairmont, W. Va., addressed the members on the subject, "Research and Chemical Education."

E. P. DEATRICK, Secretary

# OMAHA SECTION

At a meeting of the Section, held on November 6, M. V. Robins spoke on "The Weather Bureau and its Worth."

R. N. PERKINS, Secretary

## OREGON SECTION

The regular meeting of the Section was held on October 27, at Reed College, Portland, Oregon. The speaker of the evening was Arthur F. Scott, of Reed College, whose subject was "Fajans, of Munich, and Some of his Recent Contributions to Chemical Theory."

At this meeting the following officers were elected: Harry G. Miller, president; E. C. Gilbert, vice president; F. A. Gilfillan, secretary-treasurer; and R. K. Strong, councilor.

F. A. GILFILLAN, Secretary

#### PHILADELPHIA SECTION

At the first fall meeting of the Section, S. Earle Hoover, of the Hoover Construction Co., Philadelphia, Pa., addressed the members at an informal after-dinner talk urging support of the eighteenth amendment. In the evening, Henry Arnstein addressed the meeting on the subject, "The History and Practical Achievements of the Fermentation Sciences."

On November 15, Arthur Wright, of Filtration Engineers, Inc., New York City, spoke before the meeting of the Section, his subject being "Progress in Filtration and Impediments Thereto."

ELMER C. BERTOLET, Secretary

# PITTSBURGH SECTION

On November 15, R. E. Hall, of the U. S. Bureau of Mines, addressed the meeting of the Section, his subject being "Some Phases of Boiler-Water Chemistry."

E. S. STATELER, Secretary

#### PUGET SOUND SECTION

The first fall meeting of the Section was held on November 1. The speaker was Waldo Seman, of the University of Washington, his subject being "Why is an Oxime?"

W. L. Beuschlein, Secretary

# PURDUE SECTION

The second regular meeting of the Purdue Section for the year was addressed by G. H. A. Clowes, of the Eli Lilly Company of Indianapolis, Ind., his subject being "The Preparation and Properties of Insulin."

The first fall meeting of the Section occurred on October 11, when W. D. Harkins, of the University of Chicago, spoke on "The Building and Disintegration of Atoms, and the Photography of Atomic Collisions."

M. G. Mellon, Secretary

#### ROCHESTER SECTION

On October 15, Gustave W. Thompson, of the National Lead Co., spoke to the members of the Section on the subject, "Lead and Lead Compounds—A Retrospect."

The 189th meeting of the Section occurred on November 5, when Frank C. Whitmore spoke on "The Human Side of Mercury."

On November 20, the following addresses were presented before the meeting of the Section: "Science Education in the University," by Rush Rhees, president of the University of Rochester; "Science Teaching in the Public Schools," by Herbert S. Weet, superintendent of public instruction; and "Training Personnel for Chemical Control in Industry," by John A. Randall, president of Mechanics Institute.

ERLE M. BILLINGS, Secretary

#### SAINT LOUIS SECTION

A paper, with demonstrations, entitled "The Physiological Assay of Drugs," was presented before the meeting of the Section held on November 5, by E. A. Ruddiman of the John T. Milliken Co.

H. A. Carlton, Secretary

#### SAVANNAH SECTION

The Section held its first fall meeting on October 11, when the following papers were read: "The Fertilizer Industry," by Benjamin F. Taylor; and "Nitrogen Content in Chamber Acid and its Relation to the Chamber Process," by Eli H. Armstrong. Twenty-two members and visitors were present.

On November 9, R. T. Stull gave an illustrated lecture before the meeting of the Section, his subject being "Kaolin and Bauxite Deposits of Georgia and their Uses in the Arts." The annual election of officers elected at this meeting resulted as follows: John W. Everson, chairman; J. C. Howard, vice chairman; Herbert S. Bailey, councilor; Herbert P. Strack, secretary-treasurer.

Herbert P. Strack, Secretary

#### SOUTHEAST TEXAS SECTION

The 22nd regular meeting of the Section occurred on October 20. A paper entitled, "Contact Sulfuric Acid Manufacture," was read by Thomas J. Sullivan.

P. S. TILSON, Secretary

#### SOUTHERN CALIFORNIA SECTION

On November 9, William Conger Morgan, of the University of California, Southern Branch, delivered a paper before the members of the Section. His subject was "Photo Synthesis."

MARK WALKE, Secretary

# SOUTH JERSEY SECTION

Taking as his subject, "Canning," W. D. Bigelow, of the National Canners' Association Research Laboratories, Washington, D. C., addressed the meeting of the Section, held on October 18.

W. Fletcher Twombly, Secretary

#### TOLEDO SECTION

At the 56th meeting of the Section, held on October 23, Arthur Fowle, of the Libbey-Owens Glass Co., Toledo, Ohio, gave a talk on "The Manufacture of Sheet Glass."

A regular meeting of the Section occurred on November 20, when W. B. Holmes, of the Ames Laboratories, Fremont, Ohio, spoke on "The Properties of Dental Cement."

W. E. RUTH, Secretary

# UNIVERSITY OF MICHIGAN SECTION

The first meeting of the year was held on October 25, when F. G. Novy spoke on "The Pasteur Centenary."

On November 9, Frank C. Whitmore, of Northwestern University, gave an address before the members of the Section, his subject being "Recent Developments in the Organic Chemistry of Mercury."

C. C. Meloche, Secretary

#### UNIVERSITY OF MISSOURI SECTION

The regular meeting of the Section, held on October 4, was addressed by R. T. Dufford, his subject being "Luminescence of Organic Magnesium Compounds."

H. E. FRENCH, Secretary

#### VERMONT SECTION

On October 26, Marston Taylor Bogert, of Columbia University, delivered a lecture, entitled "Perfumes and Perfumery," before the members of the Section. At this meeting, the following officers were elected: Elbridge C. Jacobs, chairman; Otto Weinstock, vice chairman; Ralph R. Read, secretary-treasurer; and S. Francis Howard, councilor.

RALPH R. READ, Secretary

#### VIRGINIA SECTION

At the meeting of the Section, held on November 9, W. D. Collins, of the United States Geological Survey, gave an address, his subject being "The Industrial Value of the Soft Waters of the South."

L. C. Bird, Secretary

# WASHINGTON, D. C. SECTION

On November 8, the Section elected the following officers for 1924: R. S. McBride, president; J. B. Reed, secretary; H. W. Houghton, treasurer; Wm. M. Clark, A. Seidell, R. B. Sosman and W. W. Skinner, councilors; V. K. Chestnut, Wm. Blum, S. C. Lind, L. H. Adams, E. T. Wherry and F. W. Smither, executive committee.

J. B. Rund, Secretary

# WESTERN NEW YORK SECTION

The second meeting of the Section occurred on November 20. The speaker of the evening was W. M. Corse, of the National Research Council, whose subject was "Nickel: Its Metallurgy, Properties and Uses."

R. W. Hess, Secretary

#### DECEASED

George H. Beaumont, 2865 Fairfax Road, Cleveland, O. Died, May 12, 1923. A. R. Ledoux, 99 John St., New York City. Died, October 25, 1923. W. C. Marckworth, c/o Pure Oil Co., Columbus, O. Jacob Rosenbloom, Jenkins Arcade, Pittsburgh, Pa. Died, September 25, 1923. Arthur L. Stark, 232 East Ave., Elyriu, O.

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